Large-scale data-mining workflows are increasingly able to predict successfully new chemicals that possess a targeted functionality. The success of such materials discovery approaches is nonetheless contingent upon having the right data source to mine, adequate supercomputing facilities and workflows to enable this mining, and algorithms that suitably encode structure-function relationships as data-mining workflows which progressively short list data toward the prediction of a lead material for experimental validation.

This talk describes how to meet these data science requirements via a large-scale data-mining case study that aims to discover materials with panchromatic optical absorption for solar-cell applications [1]. In particular, the presentation shows how to auto-generate large material databases of photovoltaic-relevant experimental information from documents, using natural language processing and machine learning, via our ChemDataExtractor tool [2-4]. A workflow that executes large-scale electronic structure calculations to afford a computational counterpart to these experimental data is then described. These wavefunction calculations are used to extend knowledge beyond experiment. The resulting large database of chemical structures and their optical properties is then mined for materials discovery using custom-built algorithms that are encoded forms of structure-function relationships. These molecular design rules progressively filter the parent set of chemicals until a lead candidate appears, which is experimentally validated. The highly promising photovoltaic device outputs afforded experimentally from our predicted lead materials demonstrate the power of data-driven materials discovery.

The talk closes by translating the generic data-science aspects of this case study into the wider perspective of an overarching template for data-driven materials design, prediction and experimental validation of functional materials.

References

Despite significant progress in natural language processing and machine learning, there remains a gap between the current data extraction needs in fields such as materials science and the capabilities of state-of-the-art tools. In this talk we describe our efforts to develop human-machine methods for automatically extracting scientific facts from literature. Our overarching goal is to decrease the amount of manual extraction—a tedious, time-consuming, and error-prone process—by automating extraction activities where possible. With the assumption that our automated approaches require some supervision we seek to prioritize human involvement while optimizing overall extraction accuracy. We focus initially on the task of extracting polymer names and properties with the aim to create an outline database of polymer properties. In this context, we have explored hybrid human-machine Information Extraction systems with varied amount of human involvement.

Our recent machine learning-based approaches for automatically identifying scientific named entities in text. To circumvent the need for a large annotated corpus, we use an ensemble of word embedding models and limited domain-specific knowledge to propose candidate entities (candidates are words that are deemed similar to a reference entities by our models). We assign the labeling of these candidates (identifying strings that were not actually target entities) to an expert material scientist. This task is more straightforward than reading and recognizing the entities in documents. Finally, we train a semi-supervised named entity word vector classifier to select actual target names from candidates proposed by the word embedding model. Our preliminary results are promising as they are comparable (within 10% recall or number of entities retrieved) to results extracted by a state-of-the-art, domain-specific Natural Language Processing toolkit. However, our approach requires only minimal human input and it does not rely on an exhaustively annotated corpus.

We have assembled the largest dataset of resistivity-temperature measurements on temperature-activated metal-insulator transitions (MITs) to date (45 unique compounds). We supplemented this dataset with additional entries on metals and insulators with known transport behavior, i.e., do not undergo temperature-driven MITs, for comparison. We then collected features for the 147 compounds which describe chemical composition (e.g. mean electronegativity, atomic radii, and elemental heat of fusion); overall and local atomic structure; and estimates of the on-site electron repulsion, charge transfer energy, and compound polarizability. From this data, we constructed a machine-learning classifier to predict whether a material would undergo a MIT or not. Our model achieves a cross-validation AUC score of 88.24 +/- 11.63 and a mean accuracy of 79.23 +/- 9.23% on this metal-insulator transition prediction task. We also conducted a survey of 51 graduate students, faculty, and staff scientists to estimate the ability of scientists to classify metals vs. insulators vs. MIT. The mean accuracy for humans was 59.8%.

References

2:00 PM *GI01.02.02
Artificial Intelligence for Knowledge Generation in Materials Science

The process of scientific inquiry involves observing a signal (data) and interpreting it to generate information (knowledge). For example, in electron microscopy the signal may be a diffraction pattern from which information on crystal orientation may be deduced by applying diffraction theory. Science advances both through improvements in gathering data and in techniques for extracting knowledge from it. Artificial intelligence (AI) – a broad term comprising data science, machine learning (ML), neural network computing,
A Self-Driving Laboratory for Accelerating Materials Discovery

Kiran Vaddi, Surya Vamsi Devaguptapu, Fei Yao, Brian Hayden, Olga Wold and Krishna Rajan; Materials Design and Innovation, University at Buffalo, The State University of New York, Buffalo; New York, New York, United States; University of Southampton, Southampton, United Kingdom.

This presentation will focus on our self-driving laboratory for thin film materials discovery and optimization. Discovering high-performance, low-cost materials is an integral component of technology innovation cycles, particularly in the clean energy sector. The linear methodology currently used to develop optimal materials can take decades, which impedes the translation of innovative technologies from conception to market. Our interdisciplinary team is utilizing advanced robotics, machine learning, and computational screening to overcome this challenge. We are closing the feedback loop in thin film materials research by enabling our self-driving robotics platform named “Ada” to design, perform, and learn from its own experiments efficiently and in real time. As a proof-of-principle set of experiments, we will show how Ada discovers and optimizes high-performance, low-cost hole transport materials for use in advanced solar cells. We will also showcase how Ada’s modular design can enable the automated and autonomous discovery of materials for other clean energy technologies.
The research was conducted at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

This talk addresses the challenges of engineering a software package, which facilitates the development and deployment of the self-driving laboratories. Recently, we made significant progress towards addressing these challenges and have implemented ChemOS; a versatile, flexible, and modular orchestration software, which contains the essential layers indispensable for operating the self-driving laboratories. ChemOS coordinates the overall computational and experimental workflow, monitors experiments, administers data collection, storage and sharing as well as details about the configurations of the available automated laboratory equipment, potentially distributed across different physical laboratories. The functional design of ChemOS and its modular structure allow for the global control of complex heterogeneous automation platforms. ChemOS facilitates interaction between researchers, AI algorithms, and robotic hardware by providing various intuitive interfaces via natural language processing. One of the crucial components of ChemOS are the various AI algorithms encapsulated in the learning module. Notably, this module includes Phoenixes and Chimera, two in-house developed AI algorithms specifically designed to enable an optimal use of automated equipment for Pareto optimization in chemistry and materials science. These algorithms learn procedures on-the-fly, with no prior assumptions allowing to follow unprecedented routes to scientific discovery.

We demonstrate the performance of ChemOS on the optimization of blends consisting of hole-transport materials, stabilizers, and dopants with the goal to maximize both the conductivity and the stability of spin-coated film on glass substrate. In this example, the experimental procedure is remotely orchestrated by ChemOS, and experiments run in full autonomy.

**4:45 PM GI01.03.04**

Data Services to Increase Data Accessibility and Adoption of Data-Driven Materials Science Research

Ben Blaiszik1, Logan Ward1, Marcus Schwarting1, Jonathon Gaff3, Ryan Chard1, Zhuozhao Li2, Kyle Chard1, Yadu Nand1, Evan Pike1, Michael Franklin1, Steve Tuceke1 and Ian Foster1; 1Data Science and Learning, Argonne National Laboratory, Darien, Illinois, United States; 2Computer Science, Cornell University, Ithaca, New York, United States; 3Computer Science, The University of Chicago, Chicago, Illinois, United States.

Increasing the accessibility, application, and adoption of data-driven materials science research techniques requires a software and data service infrastructure to enable simple and broad access to large sources of materials data and state-of-the-art machine learning and physical models. For these data and models to be most useful, researchers must be able to find, access, gather, and use them. Yet datasets may be large (i.e., terabytes or gigabytes in size or comprised of millions of files), of varying qualities, heterogeneous (i.e., many file types), or located on distributed storage resources or behind varying service layers. Similarly, models of interest to a researcher may be difficult to find, completely unavailable, out of date with current data, or require a high level of technical proficiency or significant computational resources to recreate and run. Thus, building a data service infrastructure capable of simplifying and automating aspects of data and model discovery, access, and usage remains a key challenge towards speeding the pace of discovery and innovation in materials science. Here, we present a set of such data services: (1) the Materials Data Facility (MDF) to streamline broad data sharing regardless of size and location, automate materials-specific indexing of dataset contents, and enable data discovery to spur new analyses and machine learning efforts; and (2) the Data and Learning Hub for Science (DLHub) to enable publication of models, facilitate invocation of state-of-the-art models on new data through a hosted service, and automate the retraining of models when new data are available. We present the DLHub and MDF services as a means to bring data-driven materials capabilities to a much wider set of research users. These capabilities are shown via a set of examples highlighting the ways MDF and DLHub features can be combined to enable data discovery and model usage with far less effort that previously required.
more than 60 million mentions of materials, structures, properties, applications, synthesis methods, and characterization techniques from our database of over 3 million materials science abstracts. With this data, we can augment conventional materials informatics techniques with NLP-derived features, showing significantly improved performance for materials discovery and design. In particular, we illustrate that commonly used chemical features in property prediction models are outperformed by features constructed from text-mined chemical word embeddings. In addition, we demonstrate that new functional materials, such as thermoelectrics and topological insulators, can be identified using only contextualized word embeddings for materials. These embeddings also prove useful as inputs for more advanced machine learning models.

GI01.04.03
Augmenting Machine Learning of Energy Landscapes with Local Structural Information Shreyas Honrao, Stephen Xie and Richard Henning1, 2; 1Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2Materials Science and Engineering, University of Florida, Gainesville, Florida, United States.

We present a machine learning approach to calculate formation energies of compounds relative to the ground state crystal structure of the pure components in the context of structure predictions. Typical methods for structure predictions such as genetic algorithms often rely on density-functional theory codes to perform such calculations at a relatively high computational cost. Here, we explore commonly used learning algorithms such as kernel ridge regression, support vector regression, and artificial neural networks. The efficiency of machine learning approaches relies on suitable data representations that encode the relevant physical information about the crystal structures. We illustrate a novel representation using local radial and angular distribution functions. We apply the machine learning approaches to binary systems and show that these methods provide small root-mean square prediction errors of a few meV/atom across the composition and structure space. The high accuracy makes our machine learning models great candidates for the exploration of energy landscapes.

GI01.04.04
Predicting Material Properties Using a Novel Descriptor “Elemental Fingerprints” with Neural Networks Jackyun Hwang and Satoshi Watanabe; Department of Materials Engineering, The University of Tokyo, Tokyo, Japan.

Thanks to the rapid growth of machine learning (ML) techniques, it has become possible to predict various material properties, screen promising candidate materials having desired properties, and select important features. In many cases, however, a model for ML is applicable to a specific family of materials or often requires information about atomic arrangements that are difficult to obtain in real experimental situations. On the other hand, it is well known that the insufficiency in information degrades ML accuracy severely. In this study, we focus on cases where only limited information, such as a concentration of raw materials or chemical formula, is available for ML. We propose a novel descriptor set named “elemental fingerprints set” for such a situation. The elemental fingerprints set is made from the frequency distribution of properties of the elements in the target material. This set has an advantage that no information on atomic arrangements, such as crystal structure and coordination numbers, is necessary for its construction. This feature fits well with the real situation of experiments where actual atomic arrangements are not known, and only the experimental conditions and target materials are controllable. To demonstrate the effectiveness of this elemental fingerprints set, we tried to train and predict the standard formation energy, band gap energy, and volume per atom (or density) using data taken from Open Quantum Materials Database (OQMD). For materials having more than one atomic structure in OQMD, we used the most stable crystals to establish the one-to-one correspondence between materials and their properties. The models for ML were constructed using the neural network ensemble with adversarial training. This method enabled us to reduce the prediction error by more than 25% compared with a naive single neural network model. It is also worth noting that this ensemble method is suited for modern parallel computing, enabling fast training and prediction.

The elemental fingerprints set shows always better performance than the two descriptor sets suggested previously. The best performance in our study was obtained when the combination of three descriptor sets, i.e. the previous two and ours, was used together. The standard formation energy is predicted with the mean absolute error of 31.7 meV/atom and coefficient of determination of 0.981 in the test of 25,315 compounds after training with 227,838 compounds.

References

GI01.05.04
Machine Learning Accelerates the Characterization of Functional Materials Tonio Buonassisi; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

During a typical R&D cycle of learning, approximately a quarter of the time is directly invested in diagnosing the root cause(s) of underperformance, and additional time is indirectly wasted due to faulty diagnoses resulting in less productive experimental cycles. In this presentation, I demonstrate a >10x acceleration of diagnosis, with improved accuracy, using classification, regression, and advanced statics algorithms. I’ll dive deep into how classification and analysis of spectra, including X-ray diffraction data, can be performed within seconds using fully convolutional neural networks with global averaging layer, leading to an accuracy improvement of ~5% over conventional neural networks. We identify and distinguish between sources of error using class averaging maps (CAMs). This allows us to visualize the output of our algorithm, and observe what features in the spectra are used more heavily by the FCN to perform the analysis. We demonstrate that characterization problems constitute a non-trivial classification problem, by employing the t-SNE methodology, as different classes are often not linearly separable. In closing, I’ll highlight several other cases where neural networks and Bayesian inference have shed light on characterization, aiding scientists in more rapidly improving their materials.

GI01.04.06
Optimization of Transparent Hole-Conducting Materials Via Machine Learning Jingfei Wei1, 2, Xiaojie Xu1, James Bullock3, Gurudyal Gurudayal2 and Joel W. Ager1, 2; 1Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Chemistry and Chemical Engineering, Southeast University, Nanjing, China; 3Lawrence Livermore National Laboratory, Livermore, California, United States; 4Department of Electrical and Electronic Engineering, The University of Melbourne, Melbourne, Victoria, Australia; 5Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, Berkeley, California, United States; 6Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 7Materials Sciences and Engineering, University of California, Berkeley, California, United States.

P-type transparent conducting thin films (p-TCMs) are essential components of optoelectronic devices including solar cells, ultraviolet detectors, displays, and flexible sensors. Cu-Zn-S (CZS) thin films prepared by chemical bath deposition (CBD) can have both high transparency in the visible range as well as excellent hole conductivity (>1000 S cm^-1). However, the interplay between the deposition parameters in the CBD process (metal and sulfur precursor concentrations, temperature, pH, complexing agents, etc.) creates a multi-dimensional parameter space such that optimization for a specific application could be time-consuming. Here, we show that fractional factorial design of experiment (DoE) combined with machine learning allows for efficient optimization of p-TCM performance. The approach is guided by a figure of merit (FOM) related to the film conductivity and transmission T in the desired spectral range for the application (FOM, Φ = 10^{-16}RJ), where R is the sheet resistance. A specific example will be shown with 4 CBD deposition factors, leading to 62 experiments including repetitions. The machine learning model is based on Support Vector Machine Regression (SVM) employing a radial basis function (RBF) as the kernel function. 10-fold cross-validation scheme was performed to mitigate overfitting. Predicted areas in the parameter space with maximal FOMs were selected for a second round of optimization (48 experiments). Performance of optimized films as hole contacts in solar cells and in UV photodiodes will be presented. The optimization approach shown here will be generally applicable to any materials synthesis process with multiple parameters.

In case of high-throughput materials exploration, we have to treat about several hundred samples in one day. In conventional method for synchrotron powder X-ray diffraction, we have to fill fine capillaries (0.2 mmΦ) with well-grounded powder. We need more than 10 hours for only sample filling when we measure 100 sample in one day. In this study, we made a prototype for effective and high-throughput evaluation in synchrotron X-ray powder (XRD) diffraction.

Well-grounded perovskite-type Ca$_3$Bi$_2$MoO$_{12}$ powder library were set on a reaction plate (35×35×5mm$^3$), which had 36 reaction wells (diameter 4 mm and developed for high-throughput materials exploration in our group. Powder library deposited in evenly arranged wells were picked up by polyimide tape and set them to the prototype data collection tool developed as an alternative to fine capillaries. Tool were created with 3D printers. The powder adhered to the polyimide tape was made to enter the X-ray irradiation position continuously like a cassette tape.

Ideal diffraction data was obtained by swinging the tape several degrees around the irradiation position when X-rays were irradiated on the powder fixed to the tape. The lattice constant change according to Bi substitution amount can be calculated in a short time from the automatic structural analysis program developed by our group. And it was confirmed that the result was roughly the same as conventional Rietveld analysis by manual.

Acknowledgements:
These XRD and XAFS experiments were conducted at the BL5S1 and BL5S2 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Approval No.2017P0202).

G101.04.08

Distribution of Zr Atoms in Σ3(1-12)/[100] Ce$_x$Zr$_2$O$_9$ Grain Boundary Using Genetic Algorithm and Substitution Region Restriction Method
Ki-Yung Kim, Young-Bok Kim and Yeong-Choel Kim. KoreaTech, Chonan, Korea (the Republic of).

Since most technical materials are polycrystalline, it is very important to study how grain-boundaries affect the atomic distribution in crystalline materials. When Zr is added to the Σ3(1-12)/[100] Ce$_x$Zr$_2$O$_9$ grain-boundary structure to make CeO$_2$-ZrO$_2$ solid solution, the number of cases where Zr can be substituted to the Ce site is too many; in the grain-boundary structure that is composed of 48 Ce and 96 O atoms, the number of cases for 9 Zr atoms is about 10$^9$. Because added atoms are usually segregated to the grain-boundary, Mizoguchi group restricted the substitution of atoms only to atom sites around grain-boundaries and obtained an optimum structure at high speed [1, 2]. When the atoms, however, are added more than certain amount, they may start to go to bulk region. We used lattice statics and genetic algorithm to study Zr distribution in the grain boundary structure; Zr atoms gathered around the grain-boundary. We increased the structure size further to reduce the effect of grain-boundary interaction and consider the bulk region in the structure. In order to reduce the computation time, some amount of Zr atoms were first substituted to the atomic sites near the grain-boundary, and then the remaining Zr atoms were substituted to the remaining Ce sites excluding the already substituted sites in the whole Ce sites. This substitution region restriction method could help reduce the number of cases and find optimum structures at high speed.

References

G101.04.09

Construction of Neural Network Potential to Investigate Interface Structures, Ion Migration Under Electric Fields and Phonon Properties
Koji Shimizu$^1$, Takanori Moriya$^2$, Masayoshi Ogura$^3$, Wei Liu$^4$, Wenwen Li$^5$, Yasunobu Ando$^6$, Etsu Minamitani$^7$ and Satoshi Watanabe$^8$. 1Department of Materials Engineering, The University of Tokyo, Bunkyo-ku, Japan; 2Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 3Research and Services Division of Materials and Data System and Integrated System (MaDIS), National Institute for Materials Science, Tsukuba, Japan.

Recently, the construction of interatomic potentials using first-principles calculation data and machine-learning technique has been widely tried because of higher reliability and low computational costs. Our group previously constructed the interatomic potentials of amorphous-Li$_2$PO$_4$ using neural network (NN) [1], and showed that the calculated Li-ion conductivities agree well with experimental data [2]. In the present study, we have tried to extend the application range of the NN potentials (NNPs) in the following three aspects: (1) Metal/solid electrolyte interface structures (Au/LiPO$_4$ for the development of all-solid-state Li-ion batteries and novel memory devices) [3], (2) ion dynamics under electric fields (Li migration in amorphous-Li$_2$PO$_4$), and (3) phonon properties (wurtzite GaN for the power semiconductor devices).

(1) The construction of NNPs for Au/LiPO$_4$ is challenging because this is a four-elements system which involves a large number of input structures and parameters. We have explored the possibility of accelerating the construction process by the following procedure: First, we constructed two separate NNPs optimized for Au and Li$_2$PO$_4$, respectively, and then constructed the NNp for the Au(111)/Li$_2$PO$_4$ system with adding the interactions of Au-Li, P-Li and O-Li to the two NNPs. We have found that the NNPs show comparable accuracy with the conventional one, while the present approach required less computational time for NN potential optimization.

(2) The charge state is of critical importance to evaluate the change in atomic forces due to applied electric fields. By examining the forces acting on atoms in amorphous-Li$_2$PO$_4$ under electric fields using density functional theory (DFT) calculations, we have found that a proportional relationship between the changes in atomic forces and the electric field, and a strong correlation between local atomic structures and Born effective charges. Based on these findings, we have constructed the NNP which can predict the Born effective charges. In the presentation, we will also show the molecular dynamics simulation results under electric fields.

(3) Since the prediction of phonon behavior needs higher-order derivatives of energy than that of force, the accuracy of NNPs constructed with the conventional procedure [1] is often insufficient for phonon properties. Therefore we have optimized the NNPs so as to reproduce the atomic forces obtained by DFT calculations. The phonon dispersion calculated using this NNP agrees well with DFT results. In the presentation, we will also discuss the thermal conductivities of wurtzite GaN obtained by non-equilibrium molecular dynamics simulations.

This work was supported by CREST, JST and JSPS KAKENHI, Japan.


8:00 AM G101.05.01

Infrared Design of Thermoelectric Materials—Results and the Case for a Database of Charge Scattering Times
Kedar Hippalgaonkar$^1,2$; 1Institute of Materials Research and Engineering, Singapore, Singapore; 2Nanyang Technological University, Singapore, Singapore.

Deep Learning algorithms such as neural networks have recently emerged and have the potential to enable data-driven discovery of new material properties. Functional properties
are especially difficult to predict as they not only depend upon ground state properties that are routinely calculated by first principles DFT, but also transport properties such as scattering times and energy dependence. We show the first demonstration of utilizing fully connected neural networks to not only predict thermoelectric properties of the known database of materials, but also towards inverse design and feature selection for both atomic and material descriptors. The limitation of such a technique is that data on non-equilibrium descriptors such scattering times does not exist and I will talk about our foray into creating and learning from such a dataset - the Singapore Materials database (singmat) enabled by high performance computing.

8:15 AM *GI01.05.02
Pursuing the Next-Generation of High-Efficiency Phosphors with Machine Learning Jakoah Bragoch; University of Houston, Houston, Texas, United States.

The development of new phosphors that are necessary for the next generation of high efficiency LED lighting requires a unique approach for materials discovery. Researchers often rely on chemical substitution or serendipity to identify new materials; however, this inevitably leads to slow, incremental advances in technology development. Our work has recently created a new approach that uses computational chemistry and machine learning to identify new material guiding our experimental efforts. By predicting the vibrational properties and electronic structure of potential phosphors compounds, high-efficiency materials can be screened a priori ensuring the only best materials are experimentally explored. Following this methodology, our research has developed a number of materials ranging from borates to nitrides with high efficiency and thermal stability at elevated temperatures. Moreover, the complementary use of computation, machine learning, and synthesis provides a fundamental understanding of the composition, structure, and property relationship necessary for the continued advanced optical materials.

8:30 AM *GI01.05.03
Graph Networks as a Universal Machine Learning Framework for Molecules and Crystals Chi Chen1, Weike Ye2, Yuxin Zuo1, Chen Zheng2 and Shyeu Ping Ong3; 1 Nanoengineering, University of California, San Diego, San Diego, California, United States; 2 Chemistry, University of California, San Diego, San Diego, California, United States.

Fast, accurate and transferable surrogate models for property prediction have the potential to rapidly accelerate materials design and discovery. However, classical machine learning models typically depend on feature engineering and the transferability is limited in vast chemical space. Graph networks are a new ML paradigm that supports both relational reasoning and combinatorial generalization. Graphs are a natural representation for a system of atoms and the bonds between them. In addition, graph networks employ graph-level attributes to include structural independent states. Here, we develop, for the first time, MatErials Graph Network (MEGNet) for accurate property predictions in molecular and crystalline materials. We show that the MEGNet models outperform existing ML models in 11 out of 13 properties of the QM9 molecule data set. Furthermore, a single-task MEGNet model can accurately predict internal energy, enthalpy and free energy using temperature, pressure and entropy as graph-level inputs. Similarly, the MEGNet models trained on ~60,000 crystalline materials achieved significantly lower errors compared to the state-of-the-art models on formation energy, band gap and elastic moduli. Such MEGNet models are interpretable and well-known chemical trends of elements can be extracted from the model-learnt elemental embeddings. Lastly, we demonstrate that transfer learning of elemental embeddings trained from a larger data set can accelerate the training of property models with smaller amounts of data, addressing one of the critical bottlenecks to application of machine learning in materials science.

8:45 AM *GI01.05.04
Automated Machine Learning Applied to Diverse Materials Design Problems Anubhav Jain; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

There have been many recent machine learning efforts aimed at determining composition-property or structure-property relationships. Typically, each application and data set requires fitting its own model. In this presentation, I will describe a general algorithm called “automatminer” that automatically determines a machine learning model for composition-property or structure-property relationships given a data set. Automatminer generates materials science descriptors, performs feature selection, and conducts model and hyperparameter optimization all as a “black box” process. With automatminer, no user intervention is necessary to form a machine learning model. I will report automatminer's performance on a diverse array of materials data sets reported in the literature, showing performance that is comparable to or exceeds that of hand-tuned models for many different types of problems. In addition to its applications as a quick and easy way to generate machine learning models for materials, automatminer can serve as a consistent benchmark against which to evaluate the predictive power of new methods.

9:15 AM *GI01.05.05
JARVIS-ML—Physics Inspired AI for Fast and Accurate Screening of Materials Kamal Choudhary, Brian DeCost and Francesca Tavazza; Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

One of the main difficulties in applying AI to Material Science is choosing effective descriptors for materials. In this work we developed a complete set of chemo-structural descriptors to significantly extend the applicability of machine-learning (ML) in material screening for multicomponent systems. These new descriptors allow differentiating between structural prototypes, which is not possible using the commonly used chemical-only descriptors. We developed ML models for formation energies, bandgaps, static refractive indices, magnetic properties, modulus of elasticity, k-point integration grid and plane-wave cutoffs for 3D materials as well as excitation energies of two-dimensional (2D) layered materials. We used a gradient boosting decision tree (GBDT) algorithm and the training data consisted of 24549 bulk and 616 monolayer materials taken from JARVIS-DFT database. JARVIS-ML allows to make on the fly prediction using machine learning models trained using our JARVIS-DFT database.

9:45 AM BREAK

SESSION GI01.06: Automation of Materials Research—Synthesis and Characterization

Session Chairs: Jason Hattrick-Simpers and Santosh Suram

Wednesday Morning, April 24, 2019  
PCC West, 100 Level, Room 102 C

10:15 AM *GI01.06.01
Active Learning Driven Mapping of Combinatorial Libraries of Functional Materials Ichiro Takeuchi; University of Maryland , College Park, Maryland, United States.

Over the years, the challenges in the high-throughput combinatorial experimentation has evolved from synthesis of large number of disparate compounds to developing quantitatively accurate rapid characterization tools to analysis and digestion of large amount of data churned out by the methodology. To address the last challenge, we have been increasingly relying on machine learning techniques including pattern recognition within diffraction data to construct phase diagrams and mining experimental databases to look for trends in materials properties for future predictions. We have previously demonstrated on-the-fly analysis of synchrotron diffraction data, so that a rough picture of the structural phase diagram is attained immediately after all the measurements have been carried out. We are now developing techniques to let the algorithm dictate the sequence of experiments in order to maximize attainable knowledge, minimize experimental resources, and as a result further speed up the materials discovery procedure. In this active learning exercise, a Gaussian process is used to steer the mapping of combinatorial libraries. Examples of dynamic mapping of structural phase diagrams performed at a synchrotron beamline as well as with an in-house diffractometer with a variable temperature stage will be discussed. This work is performed in collaboration with A. Gilad Kusne, V. Stanev, A. Mehta, B. DeCost, J. Hattrick-Simpers, and Y. Liang, and it is funded by NIST and ONR.

10:45 AM *GI01.06.02
Exploring the Materials Genome Through Nanomaterial Megalibraries Chad A. Mirkin; Department of Chemistry and International Institute for Nanotechnology, Northwestern University, Evanston, Illinois, United States.
Throughout history, the materials we have used and rely on have evolved over time, slowly becoming more and more complex. The progression from the stone tools used by early-man to the polymeric materials used today has been relatively slow due to the massive parameter space that materials encompass. Indeed, when one considers the 91 metal elements in the periodic table, and all possible combinations, a nearly infinite number of possible materials exist. This is particularly true at the nanoscale where small changes in size or shape, even at a fixed composition, can dramatically change a material’s properties. Computational methods, or data mining of the current materials genome, can narrow the parameter space to areas of interest for a specific reaction, but experimental methods of fabricating and analyzing these nanomaterials in a high throughput manner are still required, as they often exhibit properties different from their bulk-scale counterparts. In this presentation, an approach to combinatorial nanoscience relying on “megalibraries” consisting of as many as 5 billion positionally encoded nanoparticles will be described. The libraries can be tailored to encompass a wide variety of alloy and phase-separated nanoparticles that are comprised of as many as 8 different elements. Importantly, one megalibrary contains more new inorganic materials than scientists cumulatively have produced and characterized to date. From these libraries, important insight into how thermodynamic phases form in polyelemental nanoparticles has been obtained, and design rules for engineering heterostructures in a polyelemental nanoparticle have been identified. The libraries were used to megalibarize to identify new materials and catalysts for important chemical transformations will be presented. The resulting data sets created by this platform are enormous and require new methods of analyzing them in order to decipher the implications of polyelemental nanomaterials for a wide range of applications. Therefore, this novel approach lays the foundation for creating an inflection point in the pace at which we both explore the breadth and discover the capabilities of the materials genome.

11:15 AM GI01.06.03
Generating the Largest Experimental Materials Database and Initial Findings on the Science It Enables
John M. Gregoire; Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California, United States.

In an era of rapid advancement of algorithms that extract knowledge from data, the importance of data and metadata management is more important than ever. The largest and most well annotated solid state materials databases are based on computational results, which have enabled successful implementations of machine learning in materials research. Experimental materials databases for specific data types, such as powder diffraction patterns, have been developed, but the challenges in managing and linking data across disparate synthesis and characterization experiments have hampered establishment of large databases with heterogeneous data. The recently published HITEM (Zakutayev 2018) comprises a notable advancement in this area with its well-organized and searchable database of primarily optoelectronic and structural properties of thin film materials. We present a complementary effort with measurements based on photoelectrochemistry research using methods including XRD, XRF, Raman, UV-vis, and electrochemistry. By developing a lightweight data management framework that is generally applicable for experimental science and beyond, we have compiled 5 years of experiments to produce the Materials Experiment and Analysis Database. MEAD contains raw data and metadata from ~15 million experiments on ~1 million materials, as well as the analysis and distillation of that data into property and performance metrics via software in an accompanying open source repository. The unprecedented quantity and diversity of experimental data is searchable by experiment and analysis attributes generated by both researchers and data processing software. The search web interface allows users to visualize their search results and download zipped packages of data with full annotations of their lineage. As the world’s largest open source materials database, MEAD provides substantial challenges and opportunities for incorporating data science in physical sciences, and the associated data and algorithm management framework will foster integrated incorporation of automation and autonomous discovery in materials and chemistry research.

11:30 AM GI01.06.04
Reversible Perovskite Electrocataysts for Oxygen Reduction / Oxygen Evolution for Fuel Cells and Metal-Air Batteries
Brian E. Hayden1, Kieren Bradley2, Kyriakos Giagloglou2, Hugo Jungas3 and Chris Vian4; 1University of Southampton, Southampton, United Kingdom; 2‘Uliko Technologies, Southampton, United Kingdom.

The identification of electrocatalysts mediating both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are prerequisite for the development of reversible fuel cells and rechargeable metal-air batteries. The question arises as to whether a bifunctional catalyst, or a single catalyst site, will exhibit potentials converging to the equilibrium potential of +1.23 V_RHE. Transition metal-based perovskite provide tunable catalysts where site substitution can influence both the ORR and OER catalytic activity. However, substitution in the pseudo-binary phases results in an anti-correlation in ORR and OER activities. We reveal that for LaMnNiO4 compositions with lanthanum A-site sub-stoichiometry exhibits reversible activity correlating with the appearance of the Mn3+/Mn4+ redox couple. The Mn3+/Mn4+ couple is associated with Mn5+ co-existing with Mn3+ in the bulk, as La3+ is substituted by Ni2+ at the A-site to create a mixed valent system. We also show that a direct A-site substitution by the Ca2+ cation in LaCa1-xMnO3 perovskites also results in the creation of Mn5+, the appearance of the Mn3+/Mn4+ redox couple, and a concomitant reversible activity. These results would only have been accessible with an effective combinatorial synthetic and comprehensive high-throughput screening strategy, and highlight a general strategy of optimizing oxide electrocatalysts with reversible activity.

SESSION GI01.07: Accelerating Materials Research with Machine Learning II
Session Chairs: Muratahan Aykol, Elsa Olivetti and Logan Ward
Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 102 C

1:30 PM GI01.07.01
Predicting Properties is not Enough—Realizing the Full Potential of Machine Learning in Materials Discovery
Bruce Meredith; Citrine Informatics, Chicago, Illinois, United States.

Much attention in the materials informatics community has centered on developing machine learning (ML) models to predict materials properties, based on training data derived from experiments and simulations. While such models can be helpful tools, they are (on their own) not sufficient to enable real-world materials discovery. Furthermore, the ongoing focus on property prediction creates the risk that we miss out on the value ML can provide across other critical aspects of the materials discovery process. In this talk, we discuss ML considerations beyond property prediction for materials discovery, including ML model trustworthiness and applicability, automated data analysis, and substitution of simulations or quick experiments for time-consuming, expensive characterization.

2:00 PM GI01.07.02
Design of Molecules with High Hole Mobility by Applying Machine-Learning Technologies
Nobuyuki N. Matsuzawa1, Hideyuki Arai1, Masaru Sasago2, Eiji Fujii2, Erinn Anton2 and James Saal2; 1Panasonic Corporation, Osaka, Japan; 2Citrine Informatics, Redwood, California, United States.

Materials exhibiting higher mobilities than conventional organic semiconducting materials, such as fullerenes and fused thiophenes, are in high demand for applications such as printed electronics. For hole conducting materials, derivatives of benzothieno[3,2-b][1]benzothiophene are known to exhibit the highest hole mobility, yet their carrier transport performance is still not satisfactory. The FUELS sequential learning framework was used to explore new molecules that might show improved mobility using a machine-learning (ML) guided approach. An initial ML model was trained on a set of DFT calculated hole mobilities of molecules in the amorphous state, based on the percolation treatment as derived by Evans et al. [3] According to the sequential learning process, the ML model is used to identify promising candidate molecules, hole mobilities of the candidate molecules are then calculated by applying the DFT method, and the new data are added to the training set to improve the ML model. This iterative loop was performed for several tens of times. Through this process, over 1 million candidate structures were evaluated, and about 100 DFT mobility calculations were performed. New candidate molecules having a fused thiophene structure were identified which had DFT calculated mobility that exceeded the maximum DFT mobility used in the training data set by 25%. Further details will be presented on the extrapolative design of molecules with improved carrier transport property.

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

In this study, we employ machine learning (ML) algorithms to predict electronic structure and transport properties of non-ideally fabricated multilayered thin film Si/Ge nanostructures. The ML model is trained on inexpensive -200 DFT calculations of Si6Ge1-x substitutional alloys: the training data set is populated exploiting the relationship between geometrical features or local atomic environments in these systems and their electronic structure properties. The predictor variables are obtained with Voronoi tessellation approach and the response variables are calculated with the decision tree regression algorithm. [1] This approach has successfully predicted formation energies to expedite materials discovery. [2] Our ML model trained on random alloys, has shown remarkable ability to predict electronic band structures and Onsager electronic transport coefficients of large non-ideal thin film Si/Ge superlattices. We show the predictive power of our model by comparing the predicted band structures learned from small 16-atom alloy unitcells with the electronic states of large Si/Ge superlattices unfolded to 4x4 monolayer superlattice Brillouin zones [3]. The ML framework has been especially effective in capturing crucial trends in electronic properties for a range of multilayered structures. Our ML framework will facilitate the development of inverse design approach to engineer interface profiles of integrated semiconductor architectures, to accomplish desired device performance and functionalities. The project is funded by the DARPA (DSO) MATRIX program. This work used XSEDE, which is supported by NSF grant number ACI-1053575.

Segmentation in 3D Atom Probe Tomography Using Deep Learning-Based Edge Detection

Sandeep Madireddy, Ding-Wen Chung, Troy Loeffler, Olle Heinonen, Prasanna Balaprakash, and David Seidman

Atom probe tomography (APT) facilitates nano- and atomic-scale characterization and analysis of microstructural features. APT is well suited to study the interfacial properties of granular or heterophase systems. Traditionally, the identification of the interface between, e.g., precipitate and matrix phases, in APT data has been obtained by extracting iso-concentration surfaces. These surfaces are constructed based on the marching cubes algorithm, which extracts an iso-surface from a discrete scalar field with a user-specified concentration value, or by manually perturbing the concentration value until the iso-surface qualitatively matches the interface. These approaches are rather subjective, not scalable, and may lead to inconsistencies due to local composition inhomogeneities.

We propose a digital image segmentation approach based on the holistically-nested edge detection (HED), an end-to-end edge detection approach that performs image-to-image prediction (i.e., takes an image as input, and outputs the prediction at each pixel). This is obtained using deep learning models that leverage fully convolutional networks (FCN) and deeply supervised nets. A key challenge in using deep learning approaches for our task is a lack of large amounts of ground truth segmentation data for training. We mitigate this by adopting a transfer-learning approach, where the weights in the convolution layers are initialized using a VGGNet model pre-trained on Imagenet data, and then training the HED model on the Berkeley Segmentation Dataset and Benchmark (BSDS500) dataset; both of these datasets consist of annotated natural images. The trained HED model is then used to automatically segment the data obtained from APT into different phases. Thus, this approach not only provides an efficient way to segment the data and extract interfacial properties, but also does so without the need for expensive interface labeling for training the segmentation model.

The APT data are prepared for segmentation by converting them from a 3D point cloud to a regular voxel grid composed of relative atomic concentrations of species. The trained HED model is used for interface detection on this 3D concentration space by extracting 2D slices of it in each of three orthogonal directions, detecting the 2D edges on them, and then merging all of them to obtain an edge map in 3D. The obtained edge map serves as the interfacial surface between the two phases.

We demonstrate the proposed segmentation approach using three material systems with inclusions of a precipitate phase in a matrix, each with different interface modality (layered, isolated, and interconnected, respectively), that correspond to different relative geometries of the precipitate and matrix phases. We demonstrate the accuracy of our segmentation approach through qualitative visualization of the interfaces as well as through quantitative comparisons with proximity histograms obtained using traditional approaches. We also note that the edge detection on multiple 2D slices and hence the 3D edge map extracted using the trained HED model for each of these cases is near real-time, taking only a few seconds.

Our approach demonstrates the power of machine learning techniques in the analyses of APT data. It should also be readily applicable to analysis of other tomographic data of multi-phase or multi-grain systems, such as X-ray tomography of alloy systems, or transition electron microscopy tomography. By using transfer learning the fully convolutional network can be trained in advance of experiments, and be applied in real time during the conduction of experiments. This may be especially valuable not only for 3D APT and transmission electron microscopy tomography but also for X-ray tomography, where rapid data analysis during the experiment may provide valuable real-time feedback to the experiment.
world a better place, the PSU college of engineering is seeking to make to more transformational increases in the number of women engineering graduates. This activity leverages the success of WEP and engages academic programs to provide compelling student experiences to draw interest from women and other persons from groups underrepresented in engineering. Success towards equity requires careful review of all programs with an eye towards inclusivity. Advancement of gender inclusion also demands that engineering programs identify and articulate the “why” for engineering majors. In addition, success requires that engineering programs establish collaborations with academic programs where gender balance must be aggressively addressed (mechanical engineering, aerospace engineering and computer science and engineering). Enacting efforts to reach aspirational inclusion goals also provides opportunities to identify descriptive programs (such as Humanitarian Engineering and Social Entrepreneurship) in which future engineers can be further inspired to use engineering practice to improve global societal outcomes.

To effectively change the face of the engineering workforce requires that colleges engage men as allies. Experience in gender balanced classrooms and engineering teams in college can help produce professional colleagues who interrupt many of the challenges currently faced by women in working environments. In this presentation we will discuss the success of WEP programs. We will describe efforts of the Gender Equity Initiative to increase the number of women to reach 50% of engineering graduates by 2026. We will also discuss new programs to help engage and graduate men and women who advance equity as allies for inclusion in the global workforce.

9:00 AM BI01.01.02
Writing Personal Stories About Thermodynamics Improves Professional Identity

Eric Jankowski, Sara Hagenah and Liz Neeley; Boise State University, Boise, Idaho, United States; The Story Collider, Washington, District of Columbia, United States.

Establishing Identity is at the core of the Chickering model of professional development and prior work has shown that underrepresented engineering students are more likely to be retained and graduated if students identify as a member of their major. In this work, we use a one-assignment intervention in a Junior-level materials thermodynamics course to test the hypothesis “Writing a true, personal story about a time thermodynamics happened improves self-identification as a materials scientist.” We measure student attitudes with a Likert-scale survey before and after the assignment. Preliminary results show that all of the attitudes surveyed, the only measurable change is an increase in agreement with the statement “I identify as a materials scientist.”

We discuss the impact of hosting a public Story Collider show with stories curated from the in-class assignment. We find that the attendees of the storytelling show were surprised to be emotionally affected by student stories, that the event catalyzed department discussions for how to better support students, and provided a unique forum for engagement between students, faculty, and the public. In aggregate, we find that narrative-focused activities have high potential to improve student self-identification with their profession through metacognition, with potential for increased retention of underrepresented engineering students. In parallel, the public storytelling events hold promise for improving culture, climate, and caring between stakeholders in a materials science and engineering department.

9:15 AM BI01.01.03
Princeton University Materials Academy for Minority High School Students, a MRSEC Education and Outreach Program

Daniel J. Steinberg and Sara Rodriguez Martinez; Princeton University, Princeton, New Jersey, United States.

During summer 2018, the Princeton Center for Complex Materials gave 16 underrepresented high school students from Trenton and Princeton, New Jersey, the opportunity to learn materials science and its influences on and from society. Lectures and labs included discussions on sustainability, including the UN’s Sustainable Development Goals, and coding from Princeton University professors and researchers. The Princeton University Materials Academy (PUMA) is an education outreach program for minority high school students and it is part of the Princeton Center for Complex Materials (PCCM), a National Science Foundation (NSF) funded Materials Research Engineering and Science Center (MRSEC). PUMA has been serving the community of Trenton for since 2002 each year providing daily lectures from Princeton Materials Science professors, workshops, tours and access to Princeton University laboratories, a glimpse into a real STEM academic environment. We have reached almost 300 students from 2002-2018, with many students repeating multiple years. 100% of our PUMA students have graduated high school and 98% have gone on for college, compared with the overall Trenton district graduation rate of 48% and a free and reduced lunch of 83%. This year, we discuss new initiatives and partnerships with Princeton’s makerspace “StudioLab”, a Princeton Council on Science and Technology space for collaboration and creation across disciplines (STEM, arts, humanities and social sciences), bringing in a coding and wearable technology production component to the program while meeting Next Generation Science Standards (NGSS). In addition to this, we will also discuss our launch of a new evaluation system with pre- and post-content and attitude tests. We also plan to share the curriculum online to enhance PCCM’s PUMA reach and to help teachers and high school students at a national level and improve diversity and accessibility in STEM.

9:30 AM BI01.01.04
Bystander Intervention as a Component of Developing an Inclusive Culture in STEM

Stephen D. Albright; Yale University, New Haven, Connecticut, United States.

Great opportunity exists for the fields of science, technology, engineering, and mathematics (STEM) by expanding the diversity of its workforce. Increasing diversity of an institution has been shown to improve education and increase productivity and profitability. However, the raw numbers of “diversity,” only tell part of the story. True opportunity lies in increasing the inclusivity of STEM environments, so scientists and engineers of underrepresented identities are not only present, but welcome and celebrated. A central piece to building inclusion in STEM must be changing the underlying culture, which for too long has been defined by only a narrow slice of humanity. There are many components to changing a culture; this work focuses on one, bystander intervention. Specifically, I will present details of a workshop custom-designed to teach graduate students methods for intervening in instances of disrespect and unprofessionalism. Over the course of two years, approximately 4,000 graduate and professional students at Yale, including 350 in STEM fields, have participated in this workshop. Through facilitated discussion of several tailored scenarios, participants are encouraged to develop a wide range of interventions, so anyone can find methods of intervening with which they are comfortable. By empowering community members to intervene in low stakes situations, they can break down ingrained disrespectful behavior that excludes those underrepresented in the community.

9:45 AM BREAK

10:15 AM BI01.01.05
Priming the Materials Science Pipeline—Research Opportunities for Community College Students

Scott D. Johnson, Paul S. Sabila, Joshua Halpern, Scott A. Sines and Tito E. Huber; Prince George's Community College, Largo, Maryland, United States; Howard University, Washington, District of Columbia, United States; LibreTexts, Davis, California, United States; Gallaudet University, Washington, District of Columbia, United States.

Community colleges and other small institutions lack the research equipment for students to do cutting edge undergraduate research. Moreover faculty tend to have a large teaching load, less time for research and also a lack of committed and/or trained students in the research labs as opposed to larger universities which have graduate students. Prince George's Community College (PGCC), a large urban minority institution, and Gallaudet University, an institution for the deaf and hard of hearing, have partnered with Howard University, an HBCU and R2 research university, for over a decade. Since 2007, three NSF grants have funded 46 ten-week summer intern positions that have been filled by minority students including women. Many students had multiple year experiences and were supported during the regular academic year.

Six faculty members from PGCC and Gallaudet were either involved with the students' research or the development of educational materials, including a LibreTexts textbook and matsci excels (interactive spreadsheets), and three new courses were developed while partnering with Howard colleagues. Gallaudet funded the remodeling of its science laboratories. Guidelines and procedures were also developed for dealing with the special needs of deaf and hard of hearing students in the laboratory. Nanotechnology related topics have been included in various courses in chemistry and physics at Gallaudet University. Howard faculty have also served as guest lecturers at PGCC and partners in successful grants from NASA and the Department of Education.

We will discuss the workings of a productive partnership that has given our students unique opportunities including five student co-authors on published papers. Tracking of student to bachelors degrees and beyond will be presented. PGCC and Gallaudet faculty publications with Howard colleagues have also been a productive endeavor, including a case where a Howard faculty member became involved in discipline-based educational research through collaborating with PGCC colleagues. PGCC has received NASA support for further engineering and support course revisions and laboratory equipment. Gallaudet University also has NASA support for research and student internships within the
How good can American science, engineering, mathematics, and technology (STEM) be when we are missing more than two-thirds of the talent? (i.e., everyone who is not white and male) The now-false and tired contention that “the statistics of small populations” is the operative reason for the slow advancement of underrepresented groups (women and people of color) in science and engineering, especially to positions of power and impact, has too often been used to deflect action that would transform the culture of STEM research—intensive institutions to one that adapts to the diversity of scientific talent endemic to all of humankind. Teaching academic survival skills, such as COACH (the Committee on the Advancement of Women in Chemistry) has done in workshops held for over fifteen years, without addressing the still-too dysfunctional culture in which one seeks to thrive has been shown to lead to minimal improvement in recruiting, hiring, and recognizing female academic chemists. As noted in coverage of these findings: “Perceptions of inequality remained constant across younger and older faculty, racial and ethnic lines, and levels of experience in administration.”[2] Similar difficulties are apparent among the scientific staff of national/federal laboratories.

So how can we change the world of science? Subvert the standard operating procedure. Create a microclimate that shows—over time—how new patterns of operation and inclusiveness yield productive, innovative science—including incorporating undergraduate researchers for full time (six-to-twelve months) of off-campus research. Use the scientific capital and street credentials accrued over time, thanks to the humane but challenging microclimate and the concomitant research productivity of one's team, to challenge the status quo with reasoned and bold arguments for change. Remember the importance of uppity behavior and applying “tipping point” mechanisms to move beyond initial reactions of dismissal to—over time—accepted inevitability (such as greeted my audacious suggestion in March 2000 to withhold federal funds from non-diversified chemistry departments through application of Title IX).[3] And do not forget market forces—the most important resource in research is smart, motivated students and the most important product of funded research is not peer-reviewed papers, but the critically thinking graduate. It is time to assemble a faculty diversity index that delineates who enters a group to do research, how long to degree, and where each student goes after leaving the group—all disaggregated with respect to gender, race, and ethnicity. This prize demographic—the STEM majors seeking a research program—can then make an informed decision with respect to which universities and departments and groups win their talents. We can then see who among the lovers of the status quo in the research-intensive universities really wants to play hardball. It is time to “out” the toxic departments and research groups.

1 Rolison heads the Advanced Electrochemical Materials Section at the U.S. Naval Research Laboratory (NRL). The views are those of the author and are not necessarily those of the NRL or the U. S. Department of Defense.


10:30 AM B101.01.06
Science is Too Important to Be Left Just to Men
Debra R. Rolison; Consultant, Arlington, Virginia, United States.

In our presentation, we will discuss each program component, our measures of success which include self-efficacy, retention results and academic performance of our freshman fellowship. Students have had socials highlighted by various activities including basketball and hockey games as well as riverboat rides. Monthly socials provide professional development opportunities for students. Students are visited by industry partners to discuss resume writing, interview tips, networking and groups and receive tutoring and academic support. The students generally perform 10-15 points higher than their counterparts. These Collaborative Courses including Calculus and Physics supplement their first-year course loads. Through the support of our programming, our students generally perform 10-15 points higher than their counterparts.

The retention program consists of 4 main components, the summer bridge program, monthly socials, collaborative math and science courses and Sunday dinners. The Summer Bridge Scholars Program is a 7-week summer bridge program. Incoming first-year students participate in a seven-week bridge program. In the program, the students live on campus and are immersed in a campus experience. They take a full course load of classes including: Calculus/Pre-Calculus, Chemistry, Biology, Engineering Design and English. The students participate in study groups and lunch and learn series to help them prepare for their first-year experience. Students who perform well in their Mathematics, Chemistry and Biology courses receive English credit that go towards their graduation requirements. In their first year on campus, the students are grouped into a cohort and provided support to transition into their academic careers. They participate in Collaborative Courses which are offered through IEEC. These Collaborative Courses including Calculus and Physics supplement their first-year course loads. Through the support of our programming, our students generally perform 10-15 points higher than their counterparts.

The office also hosts a weekly Sunday dinner. During the dinner, the students receive a home-cooked meal and have a chance to network with students in all cohorts. The dinner provides a safe space for students who are often facing stereotype threat and implicit bias in their courses. In addition to fellowship and networking, the students also work in study groups and receive tutoring and academic support. Monthly socials provide professional development opportunities for students. Students are visited by industry partners to discuss resume writing, interview tips, networking and etiquette. Many of our industry partners use this time to develop authentic relationships that feed into an informal mentoring network. We also use monthly social time for fellowship. Students have had socials highlighted by various activities including basketball and hockey games as well as riverboat rides.

In our presentation, we will discuss each program component, our measures of success which include self-efficacy, retention results and academic performance of our freshman cohort.

1:30 PM *B101.02.01
Holistic Retention Strategies for Underrepresented Minority Students
Whitney Gaskins and Dewey Clark; University of Cincinnati, Cincinnati, Ohio, United States.

A small percentage of underrepresented minority high school graduates pursue STEM majors. Often, underrepresented minority students are subjected to stereotype threats, such as being labeled as intellectually inferior, purposely not being selected to participate in classroom discussions and a lack of sense of belonging, such as a lack of inclusivity from class peers and academic advisors while matriculating through the academic programs. The Office of Inclusive Excellence and Community Engagement (IECE) has a retention program focused on increasing the retention, self-efficacy and sense of belonging of underrepresented minority students in the College of Engineering and Applied Science.

The retention program consists of 4 main components, the summer bridge program, monthly socials, collaborative math and science courses and Sunday dinners. The Summer Bridge Scholars Program is a 7-week summer bridge program. Incoming first-year students participate in a seven-week bridge program. In the program, the students live on campus and are immersed in a campus experience. They take a full course load of classes including: Calculus/Pre-Calculus, Chemistry, Biology, Engineering Design and English. The students participate in study groups and lunch and learn series to help them prepare for their first-year experience. Students who perform well in their Mathematics, Chemistry and Biology courses receive English credit that go towards their graduation requirements.

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2:00 PM *B101.02.02
Professional Societies and African American Engineering Leaders—Paving Pathways and Empowering Legacies
Christine S. Grant1, Tonya L. Peeples2 and Lynnette D. Madsen3; 1Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2Department of Chemical Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; 3National Science Foundation, Alexandria, Virginia, United States.

Diversity and inclusion in science, technology, engineering, and mathematics (STEM) fields is a global issue. The challenging issues facing the world relating to STEM diversity cross national borders and require leveraging the talents of diverse constituents. Active international efforts at inclusive talent development are being undertaken to empower persons from groups historically underrepresented in STEM communities. The US National Action Council for Minorities in Engineering (NACME) reports that in the United States, African Americans are one of the most underrepresented minority groups in engineering relative to their population. This is in spite of the fact that there has been a great deal of progress in “growing African American scientists, engineers, and technologists since the Howard University School of Engineering opened in 1910.” The number of
African Americans in engineering at all degree levels is not representative of their percentage in the US population.

In 2012, a workshop on “Ethnic Diversity in Materials Science and Engineering” was co-sponsored by the National Science Foundation (NSF), the Department of Energy (DOE), the MRS Foundation, North Carolina State University, and the University Materials Council (UMC). Comprised of Department Heads, Chairpersons, Directors, and group leaders from academic programs in the materials field in United States, Canadian, and Australian universities, UMC is a forum for sharing best practices related to materials science and engineering (MSE). Focusing on issues affecting recruitment and retention and long-term success in MSE, the workshop participants examined diversity data in MSE departments. According to the US National Center for Science and Engineering Statistics, although African Americans make up 12.2% and Latinos 16.3% of the US population, they received only 2.5% and 5.3% of MSE degrees awarded in 2010, respectively. At the heart of the recommendations to increase retention, recruitment, and career success of ethnically diverse groups were topics with a focus on the following three groups: (a) Individuals, (b) Academic Leaders, and (c) Federal Agencies.

Our goal in this paper is to shift this conversation away from the dire message about the lack of African Americans in the field and focus on positive advancements, namely, the leadership of African Americans in engineering and the role of professional societies in their leadership development. Reflecting on the action plan for ethnic diversity in MSE and STEM, we posit that there is a constituency missing in these discussions, namely, professional societies. While it is critically important to recognize technical achievements and the early champions of change, it is also crucial to highlight the importance of professional societies, and challenge them to develop a greater level of authentic inclusion of African Americans in their organizations. Societies include, but are not limited to, those focused on: (1) advancing diversity and inclusion via empowerment, (2) developing underrepresented groups within specific disciplines, (3) originating and facilitating cross-disciplinary interactions, and (4) leading change in the realm of providing services, information, and tools for stakeholders to create a diverse workforce of engineers. Professional societies can play a pivotal role in the diversification of science and engineering profession and the authentic inclusion of engaged African Americans in the direction of science and engineering disciplines. We will discuss how the development of leaders across academia, industry and governmental entities benefits from the opportunities to grow, serve and eventually lead in student-led, career-enhancing, and paradigm-shifting organizations. This paper highlights the careers of several African American leaders in both industry and academia, including their experiential perspectives on the role of professional societies in their own leadership development.

2:30 PM BI01.02.03
Implementable Group-Based Undergraduate Research Programs for First-Year STEM Students
Matthew Hauwiller, Justin Ondry, Anne Baranger and Paul Alivisatos; University of California, Berkeley, Berkeley, California, United States.

Undergraduate research has numerous positive outcomes for the participating students ranging from improved performance in classes, higher self-identification as scientists, better graduation rates, and better retention of students from underrepresented demographics. By actively carrying out cutting-edge scientific research, students feel like scientific experts with the ability to tackle difficult problems, and this sense of belonging can be especially valuable for first generation and underrepresented students. Ideally, every first-year student at large research institutions would have the opportunity to be a part of the ground-breaking research happening on their campus; however, the current models of undergraduate research are often unable to provide that experience to first-year undergraduate students. Traditional apprenticeship research positions are designed for advanced undergraduate students who want to make a significant time commitment. Course-based undergraduate research experiences have many positive benefits but often lack the ability to replicate a true research experience. We developed a research group-based undergraduate research program for first-year undergraduate students. Our program allowed 20 students to pursue curiosity driven research using cutting edge data previously collected by our research group. This model is transferable to other research groups, departments, and universities, and the implementation of first-year research experiences would be a significant benefit to the educational experience of undergraduate students, especially for students from underrepresented backgrounds in STEM.

In this program, students were given unanalyzed videos of platinum nanocrystals moving, growing, and attaching in solution collected using a state-of-the-art electron microscope and then were able to investigate and analyze phenomena they found intriguing. We assumed the students had no previous research experience nor knowledge of our research area of nanomaterials, so we taught the background information necessary to complete their projects. After learning the fundamentals of the research area, the undergraduate students began brainstorming interesting questions about the data set they were provided. Students were able to test various hypotheses for how nanocrystals grow and interact and learn how to pivot from a failed idea to a more promising hypothesis. Finally, the students learned how to communicate their results in the form of an academic paper and a poster presentation. Going through the scientific process with a project that was scientifically relevant gave the undergraduate students valuable experience as well as a sense of accomplishment.

The immediate returns, both qualitative and quantitative, show the ability for programs like AGURP to make a difference in the education experience of all first-year STEM students. Roughly half of the participants who came to the information session were women, and half of the admitted students were women. The students expressed a sense of ownership of their project at the poster session and were proud of their research achievements. Quantitatively, the students expressed significant gains in their self-identification of their research skills from the pre- and post-program surveys. For a program like AGURP to be sustainable, it needs to be positive for both the students and the research groups, and programs like AGURP can be mutually beneficial. The goal of developing a group-based research program is to build an implementable model for other universities, so every first-year undergraduate student aspiring to achieve a STEM degree can feel a sense of belonging through research and increase their persistence rate to graduation.

2:45 PM BI01.02.04
Understanding the Impact of Design in High School Outreach Camps
Kaitlin Tyler, Nicole Johnson-Glauch, Leon Dean and Jessica A. Krogstad; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

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

3:00 PM BREAK

3:30 PM BI01.02.05
Engineering Change—Strategic Action to Achieve Diversity in Engineering
Jenni M. Buckley, Stephanie Law, Amy Trauth and Rachel Davidson; University of Delaware, Newark, Delaware, United States.

The underrepresentation of women and underrepresented minorities (URM, def. non-White, non-Asian) in the engineering pipeline can be attributed to a multitude of factors, including, but not limited to, insufficient preparation and barriers in recruiting into engineering programs at the K-12 level, low self-efficacy, lack of peer support, inadequate academic advising or faculty support, harmful stereotypes of particular groups that influence interactions in classrooms or in peer groups, and a chilly or unappealing climate. The numerous “leaks” in the pipeline along with the sheer variety of established causes lead many institutions, including our own, to take a scattershot and therefore marginally effective approach to promoting diversity and inclusion.

In this paper, we will demonstrate that the Engineering Design Process (EDP) provides an effective framework for goal-setting and developing targeted interventions to substantively advance diversity and inclusion at the undergraduate and graduate levels. We present this work in the form of a 3-year case study at our own institution, a mid-sized, research-focused, land grant university on the US East Coast with student demographics (gender, racial) that reflect national trends. Our EDP framework consists of three steps: (1) Defining the Problem, (2) Developing multiple unique and viable concepts, and (3) Iteratively designing, implementing, and refining or abandoning interventions based on formative evaluations. We began in Phase 1 of EDP by defining the issue of diversity at our institution relative to other engineering programs nationally using publically available data on graduation and retention rates. To assess climate issues, we conducted in-depth focus groups of women, URM, and majority undergraduate and graduate students; and we folded the common themes from these focus groups into annual surveys. These data were used to establish clear metrics and target values for gender and racial diversity across our graduate programs and within each undergraduate department.
Phase 2 of our EDP involved generating multiple unique and viable interventions that addressed the disparities in recruitment and retention identified in Phase 1. Both working groups engaged in a lengthy phases of divergent concept generation by conducting extensive literature reviews, familiarizing themselves with the educational and social psychology literature around diversity and inclusion in STEM, and benchmarking interventions from other institutions. Early concepts were organized using a novel tool that clusters interventions by area of impact (recruitment or retention) and “activation energy” (economic and political cost).

Phase 3 of the EDP, which is ongoing as of this publication, involves implementation and continuous, formative evaluation of interventions clustered into three Specific Aims: (1) Recruitment, (2) Retention; and (3) Cultural Change. At present, the undergraduate working group has operationalized approximately 80% of the specific interventions clustered in Aims 1 and 2 above and 30% in Aim 3. Based on evaluating data, 10% of the interventions have been discontinued, with an additional 20% being substantially modified based on early results. Both working groups are continuously reviewing admissions data to assess impact on recruitment and leveraging focus group and survey data to monitor student climate.

This case study represents the first explicit use of the Engineering Design Process (EDP) to develop a comprehensive plan to address diversity and inclusion at both the undergraduate and graduate levels. Given how daunting diversity issues can sometimes appear, we have found that framing and addressing this issue like engineers and explicitly using the EDP has made the process of goal setting, intervention, and evaluation remarkably clear. The overall process and specific tools presented in this case study may be easily extended to other institutions.

3:45 PM INVITED SPEAKER - RICK

SYMPOSIUM CP01

Advances in In Situ Experimentation Techniques Enabling Novel and Extreme Materials/Nanocomposite Design
April 23 - April 26, 2019

Symposium Organizers
Arief Budiman, Singapore University of Technology and Design
Jessica Krogstad, University of Illinois at Urbana-Champaign
Nan Li, Los Alamos National Laboratory
Nobumichi Tamura, Lawrence Berkeley National Laboratory

* Invited Paper

SESSION CP01.01: Xtreme Materials Design
Session Chairs: Arief Budiman and Jessica Krogstad
Tuesday Morning, April 23, 2019
PCC West, 100 Level, Room 101 A

10:30 AM *CP01.01.01
Nanomaterials Design and Properties at the Extreme Limits of Molecular-Scale Confinement Reinhold H. Dauskardt; Stanford University, Stanford, California, United States.

We review the state-of-the-art in the molecular design and processing of nanomaterials at the extreme limits of molecular-scale confinement. A particular focus is provided on unique mechanical and electrical behavior that can be achieved in the limit of such intimate molecular mixing. We show that molecular hybrids can have marked asymmetric elastic and thermal expansion properties that are inherently related to terminal chemical groups in confinement. We describe a new nanoscale design principle using hyperconnected molecular architectures to achieve remarkable mechanical properties controlled by designing connectivity into the intrinsic molecular structure in innovative ways. We probe the mechanical and fracture properties of hybrids in the extreme limits of molecular confinement, where a stiff inorganic matrix phase confines polymer chains to dimensions far smaller than their bulk radius of gyration. Finally, we demonstrate the synthesis of 1D core-shell nanowires that have electrically conducting copper cores and insulating shells. Nanowires are synthesized via a facile solution process leveraging the strong chemical interaction between organothiol molecular precursors and copper. We use molecular dynamic and density functional theory computations together with atomic resolution characterization to reveal the molecular structure, and electrochemical impedance spectroscopy to characterize the electrical properties.

11:00 AM *CP01.01.02
Role of Graphene in Reducing Fatigue Induced Damage in Cu-Graphene Nanolayered Composite Byungil Hwang1, 2, Wonsik Kim1, Jaemin Kim1, Seoyeon Lim1, Sangmin Kim1, Sangho Oh1, Seunghwa Ryu1 and Seung Min Han1, 2, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 1Sungkyunkwan University, Suwon, Korea (the Republic of); 2BASF Electronics Materials R&D, Suwon, Korea (the Republic of).

Nanoscale metal-graphene nanolayered composite is known to have ultra high strength due to its ability to effectively block dislocations from penetrating through the metal/graphene interface. The same graphene interface can simultaneously serve as an barrier interface for deflecting the fatigue cracks that are generated under cyclic bendings. Cu-graphene composite with repeat layer spacing of 100 nm was tested for bending fatigue at 1.6% and 3.1% strain up to 1,000,000 cycles that indicated ~5 times enhancement in robustness against fatigue induced damage in comparison to the conventional Cu only thin film. Fatigue induced cracks that are generated within the Cu layer were stopped by the graphene interface, which was confirmed using transmission electron microscopy images acquired ex-situ as well as during in-situ tensile strain testing. Molecular dynamics simulations for uniaxial tension of Cu/Gr showed limited accumulation of dislocations at the film/substrate interface, which makes the fatigue induced crack formation and propagation through thickness of the film difficult in this materials system.

11:30 AM *CP01.01.03
From Nano to Macro Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent advances in nano-manipulation, environmental TEM and MEMS allow us to investigate coupled mechanical and electrochemical phenomena with unprecedented spatial and temporal resolutions. For example, we can now quantitatively characterize liquid-solid and gas-solid interfaces at nm-scale. These experiments greatly complement our modeling efforts, and together they help provide insights into how materials are transformed in synthesis and how they behave in service due to combined electrochemical-mechanical forces. Applying theory, modeling and lab-on-a-chip microscopy, together with cost modeling, can judiciously guide the scalable production of high-performance energy materials.
SESSION CP01.02: Xtreme Materials Design Applications—Wearables and Microrobotics
Session Chairs: Arief Budiman and Young-Chang Joo
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 101 A

1:30 PM *CP01.02.01
Development of Reliable Wearable Electronic Devices Through In Situ Monitoring Young-Chang Joo, Seoul National University, Seoul, Korea (the Republic of).

Flexible and stretchable devices are of significant interest due to their potential expansion of the application of smart devices into various fields, such as energy harvesting, biological applications and consumer electronics. Due to the mechanically dynamic operations of such electronics, their mechanical reliability must be thoroughly investigated to understand their failure mechanisms and lifetimes. Reliability issue caused by bending fatigue, one of the typical operational limitations of flexible electronics, has been studied using various test methodologies; however, electromechanical evaluations which are essential to assess the reliability of electronic devices for flexible applications had not been investigated because the testing method was not established. By employing the in situ fatigue test, we have studied the failure mechanism for various conditions and parameters, such as bending strain, fatigue area, film thickness, and lateral dimensions. Moreover, various methods for improving the bending reliability have been developed based on the failure mechanism. Nanostructures such as holes, pores, wires and composites of nanoparticles and nanotubes have been suggested for better reliability. Flexible devices were also investigated to find the potential failures initiated by complex structures under bending fatigue strain. The recent advances in test methodology, mechanism studies, and practical applications are introduced. Additionally, perspectives including the future advance to stretchable electronics are discussed based on the current achievements in research.

2:00 PM *CP01.02.02
Nano-Chemomechanics at Play—Novel Nickel-Hydroxide Thin-Film Actuating Materials for Micro-Robotics Applications Alfonso H. Nguyen, Runni Wu and Kenneth K. Kwan; University of Hong Kong, Hong Kong, Hong Kong.

In this talk, we report a novel actuating material—nickel hydroxo-oxyhydroxide—that exhibits enormous actuation due to a volume change stimulated either electrochemically, or by illumination of visible light of low intensities. For electrochemical actuation, Ni(OH)2/NiOOH is capable of undergoing fast, reversible, and large actuation in alkaline electrolytes under potentials of less than 1 V, due to a redox reaction involving volume changes. On the other hand, the light actuation of Ni(OH)2/NiOOH is due to its turbostratic crystal structure which is capable of intercalating water molecules. It is shown that the intercalated water can be rapidly and reversibly desorbed into the environment under visible light of intensities lower than 1 sun, resulting in fast actuation driven wirelessly by light.

By electroplating the actuating material on passive substrates, we have fabricated film-actuators capable of undergoing reversible bending and curling with an intrinsic actuating stress of tens of megapascals at response rates in the order of tens to hundreds of degrees per second, which are comparable to mammalian skeletal muscles. Also, by intentionally electroplating the nickel hydroxo-oxyhydroxide on selected areas of the substrate, we have also fabricated actuation devices of various shapes and functions, e.g. a hinged actuator that can lift objects ~100 times of the weight of the actuating material is achieved, and other examples showing the potential use in robotic devices. The light-induced actuation mechanism reported here has the potential for realizing wirelessly powered micro-robotic devices.

2:30 PM CP01.02.03
A Highly Sensitive and Selective Relative Humidity Sensor Based on Mn Loaded Cubic Mesoporous SBA-16 Vijay K. Tomer1, Jasbir Sangwan1, Vijay Kiran1 and Ekta Poonia2; 1Department of Higher Education, Government of Haryana, Tau Devi Lal Govt. College for Women, Sonipat, India; 2Berkley Sensor and Actuator Center, University of California, Berkeley, Berkeley, California, United States; 3Chemistry, CRA College, Sonipat, India; 4Chemistry, D.C.R. University of Science and Technology, Sonipat, India.

The template assisted facile synthesis of 3-D cubic mesoporous silica comprised with in situ doping of metal oxides, immense surface to volume ratio, ordered network of long range porosity and ultrafine size was proposed in this study. The FE-SEM and HR-TEM studies indicated the novel morphology of hexagonal cubic channels with ordered network of porosity, X-ray diffraction study confirmed the 3-D cubic structure of silica with existence of anatase phase of in situ doped metal oxide species containing Im3m symmetry. N2-BET adsorption desorption isotherm displayed the immense surface area (768m2/g) of synthesized material which was decreased (715m2/g) after in situ doping of metal oxides due to decrease in mesoporous volumes. The sensing behavior of synthesized nanostructures was determined by measuring the change in impedance corresponding to different RH conditions. The in situ doped metal oxide silica samples specified a swift response time of 4.7 s and quick recovery time of 3.2 s exhibiting synergistic effect as compared to undoped silica. In addition, the long term stability, sensitivity, great recyclability and less hysteresis indicated the possible practical application of synthesized nanoparticles.

2:45 PM CP01.02.04
Nanoscale Dielectric Charging and Breakdown Mapping Thomas Moran1, James Steffles1, Keigo Suzuki2 and Bryan D. Huey3; 1University of Connecticut, Storrs, Connecticut, United States; 2Murata Manufacturing Co., Ltd., Yusa, Japan.

Dielectric thin films are crucial for counting, computing, wireless, and sensor systems. As their dimensions continue to diminish, and engineered microstructure becomes increasingly refined, it is crucial to be able to investigate charging, discharging, and breakdown at the nanoscale. Based on Atomic Force Microscopy several new approaches have been developed for such investigations, reported here for BaTiO3 as well as BaTiO3 and SrTiO3 superlattices. In this manner, the influence on charging and discharging can be mapped for grain boundaries as well as heterostructure interfaces. Furthermore, by applying voltages up to 150V, in a controlled environment, across films shallow-angle-polished to create thicknesses gradients from 200 down to 2 nm, scaling laws for breakdown become uniquely accessible on a single specimen. This is advantageous as the composition is reasonably consistent, as comparable to investigations with multiple films. Such methods are equally applicable for investigations of breakdown mechanisms with inorganic as well as polymeric dielectrics.

3:00 PM BREAK

3:30 PM CP01.02.05
In Situ Raman Spectroscopy to Study Plastic Deformation in Silicate Glasses Shefford P. Baker1, Nicole Wiles1, Zachary Rouse1, Praveena Manimunda2, Thomas Wyrobek1 and S.A. Syed-Axil2; 1Cornell University, Ithaca, New York, United States; 2Bruker Nano Surfaces, Minneapolis, Minnesota, United States.

Understanding plastic deformation in silicate glasses is important in the development of glasses with improved resistance to mechanical failure. Plastic deformation under a point contact determines the stress state, which determines whether a surface flaw forms, which in turn determines the strength of the glass. Unfortunately, relatively little is known about the atomic scale mechanisms that control plasticity in silicate glasses. To date, most effort has focused on the continuum concepts of shear and densification. Raman spectroscopy has been used to study structure of glass glasses deformed by indentation and indentation. To investigate the structure of plastically deformed glass under load, we have developed an instrument in which the deformed material under the indenter can be investigated in-situ, while the load is being applied. Measured changes in spectra can be correlated to changes in ring size, bond angles, and other structural motifs with load. Transient structural changes which disappear after load is removed were identified.

3:45 PM CP01.02.06
Direct Observation of Conducting Channels in SrCoO3, Based RRAM Device Hung-Yang Lo, Juan-Min Huang and Wen-Wei Wu; National Chiao Tung University, Hsinchu, Taiwan.

Resistive random access memory (RRAM) has attracted considerable interest for next-generation non-volatile memory due to its fast switching speed, high storage density and excellent scalability. To effectively control the switching characteristic with considerable memory performance, a complete study of the switching behavior is essential. In this work,
we utilize SrCoO₃ (SCO) which grows on Nb-doped SrTiO₃ (Nb-STO) substrate as our dielectric layer since it exhibits large different resistance between SrCoO₂₋ₓ and SrCoO₂₋ₓ, where the value of SrCoO₂₋ₓ is higher than that of SrCoO₃. Based on this characteristic, we fabricated a Au/SCO/Nb-STO device, and measured the SET (~1.6 V) and RESET (~−5.3 V) process with more than 700 cycles. Meanwhile, the conducting filaments were observed via in-situ transmission electron microscope (TEM). From the HRTEM results and corresponding FFT-DP (Fast-Fourier-Transform Diffraction pattern), it is clearly demonstrated the formation of conducting filaments is from SrCoO₂₋ₓ to SrCoO₂₋ₓ. Accordingly, the formation/rupture of conducting path is due to the movement of oxygen vacancy, and hence its resistance is able to switch reversibly between low resistance state and high resistance state. This study not only revealed the switching mechanism of SrCoO₂, but also proved it to be the promising candidate for RRAM application.

SESSION CP01.03: Advances in Xtreme Experimentation I
Session Chairs: Arief Budiman and Ralph Spolenak
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 101 A

4:00 PM CP01.03.01
Shining Light on Nanoscale Mechanical Properties Ralph Spolenak
ETH Zurich, Department of Materials, Laboratory for Nanometallurgy, Zurich, Switzerland.

When investigating films thinner than one hundred nanometers, X-ray diffraction at synchrotron sources has been the method of choice in order to achieve enough signal. When films, however, exhibit a nanocrystalline microstructure and consist of light elements also diffraction reaches its limits. Here we provide case studies on reflection anisotropy spectroscopy that is sensitive to elastic distortions of the lattice or the symmetry breaking of a crack pattern. Thin films only start reflecting less than their bulk counterparts, when their thickness reaches several tens of nanometers and thus experiments can be extended to the single digit nanometer thickness regime. The case studies focus on plastic deformation and fracture on the phase change media as well as colored and noble metal thin films for applications in wearable electronics.

4:30 PM CP01.03.02
Direct Observation of Metallic NPs Electrodeposition on Glassy Carbon (GC) and CNTs by In Situ and Operando TEM Flores L. Ileana 1, Mariam Ezzedine 1, Leandro Sacco 1, Mihai R. Zamfir 1 and Costel Cojocaru 1, 2; 1 Ecole Polytechnique, Palaiseau, France; 2 CNRS, Palaiseau, France.

Liquid electron microscopy is a new TEM-based characterization tool that allows us to apply the powerful capabilities of an electron microscope to probe image and understand real-time nanoscale morphological and structural evolution of nano-systems under certain electrochemical conditions (operando).[1] For in situ electrochemical experiments, the importance of using the liquid cell is related to the fact that experiments in liquid environments enable direct imaging of the key phenomena taking place during the battery operation, stage crucial for establishing a good correlation between the microstructure of nanocomposites and the performance of the device. The main challenge of our work is the assessment of the batteries performances when nanostructured electrode materials are considered for both the anode and the cathode. Nanostructured materials show great promise; they can open new possibilities for enhancing the energy density of Li-ion batteries. The present study is focused on the realization of the in - situ liquid TEM observation using a closed electrochemical cell [2] of the electrochemical technique that activate the nanoparticle nucleation/growth mechanism of under certain electrochemical conditions (operando) as the ionic solution is introduced into the cell(unit) [3, 4]. From the experimental point of view, two electrodeposition approaches have been used: the cycling voltammetry and pulsed chronoamperometry modes both under constant flow. The interpretation and the analyses of the recorded current versus time curves allowed us observing that the nucleation mode is strongly related to the deposition conditions. Thus we noticed when the pulsed chronoamperometry mode is used we have a homogeneous NP deposition on the working electrode. The NPs size is depending on the cycle number and the liquid flow rate within the cell. In contrast, under cycling voltammetry mode, we observe an inhomogeneous deposition of the NPs generated by the oxidation of different organic species that can be formed after the first cycle.


SESSION CP01.04: Poster Session: Advances in In Situ Experimentation Techniques Enabling Novel and Extreme Materials/Nanocomposite Design
Session Chairs: Arief Budiman, Jessica Krogstad, Nan Li, Nobumichi Tamura and Nobumichi Tamura
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

CP01.04.01
Synthesis and Interfacial Analysis of Carboxyl Functionalized Carbon Nanotube - MOF-808 Composite Using Scanning Transmission Electron Microscopy (STEM) Justin W. Hendrix; Naval Surface Warfare Center, Dahlgren Division, Dahlgren, Virginia, United States.

Carbon Nanotubes (CNTs) and Metal Organic Frameworks (MOFs) represent two of the most promising classes of emerging materials in engineering today. Together, they exhibit many useful properties such as high conductivity [1], catalytic reactivity [3], porosity [4], and strength [2]. Methods in integrating these materials towards electromagnetic and chemical applications is of strategic importance for defense. Innovative materials have often been designed by combining low and high dimension constituents, through compositing, as a means to improving the functionality. In this work, we were able to combine these nanomaterials by synthesizing novel MOF-CNT nanostructured composites, using zirconium containing MOF (MOF-808). MOF-808 is composed of zirconium (IV) nodules, connected by organic carboxyl linkers, to create a nanoporous octahedral 3D crystal structure. Carboxylated functional groups are believed to be an important surface modification, due to its ability to bridge the zirconium nodules. Multiwalled CNTs, surface functionalized with carboxyl end groups, were used as the reinforcing agent with MOF-808 to create a MOF-CNT composite. The functionalities were chosen to create a MOF-CNT composite, linked by primary bonds. Scanning transmission electron microscopy (STEM) and nanoarea electron diffraction are powerful techniques in identifying structural changes at atomic scale resolution. Using a NION UltraSTEM-200X and a JEOL 2200FS at the U.S Naval Research Laboratory, we are able to identify MOF-808 adhesion to the surfaces of functionalized CNTs. Analysis shows the existence of lattice defects at the interface of MOF-808, as synthesized with carboxylated CNTs. The disruption is believed to be caused by the carboxylated CNTs acting as heterogeneous nucleation sites, forming the MOFs around the nanotube center. In this work, STEM and electron diffraction are used as effective techniques to study the interface of surface modified nanostructure composites.

doi: 10.1109/MOCAST.2018.8375600
Development of Compound Melt Extruded Nanocomposite FDM Filament by Continuous Syringe Pumping of Dispersed Graphenes During the Extrusion

Dripping water on to the polymer melt did not lower the degradation temperature of any of the polymer, indicating it evaporates off immediately as intended. Mechanical strength was seen to improve by 20% in composites of PLA/EFG at 8wt%, and by 10% in dual filler composites PLA/EFG/LCGO at 2wt%. Direct solution addition mid extrusion has shown to generate average agglomerate size range from <500nm to 50μm. It is expected that the upper limit will lower to 25μm with a slower addition of filler. Powdered polymer (HDPE/LDPE/PLA) was added to the first port of the extruder. Once the polymer was molten, a dispersion of fillers (LCGO/EGF/laponite) in an aqueous solution was syringe pumped directly into the melted polymer in a second port along the extrusion screw. As each drop of solution was added, the water evaporated and the filler was taken in to the polymer. This method prevents a lot of the filler-filler contact that occurs in typical powder coating methods, which in turn keeps agglomerate size low. Solution concentrations were up to 10mg/mL, added at at 6mL/min. LCGO was made on site at UOW [4], to approximately 9mg/ml (aq. dispersion). EGF was made in house at UOW. Laponite was sourced from BYK Additives and Instruments (Germany). PLA was sourced from Filabot (USA), HDPE from Sigma-Aldrich (USA), LDPE from Visy (Australia). Each additive was diluted to 0.1, 0.5, 1, 2, 5 and 10mg/mL in an aqueous solution for both single and dual filler composites. Direct solution addition mid extrusion has shown to generate average agglomerate size range from <500nm to 50μm. It is expected that the upper limit will lower to 25μm with a slower addition of filler. Mechanical strength was seen to improve by 20% in composites of PLA/EFG at 8wt%, and by 10% in dual filler composites PLA/EFG/LCGO at 2wt%. Dripping water on to the polymer melt did not lower the degradation temperature of any of the polymer, indicating it evaporates off immediately as intended.

Acknowledgements
The authors thank the Australian National Fabrication Facility - Materials Node for their provision of research facilities, acknowledge the use of facilities within UW Electron Microscopy Centre and funding provided by the ARC Centre of Excellence for Electromaterials Science.

References:
plastic relaxation and formation of martensite resulting from the transformation induced plasticity (TRIP) effect. The (BF+RA)nanostructure nucleated at PM interface shows more pronounced resistance to cyclic deformation and leads to the fatigue crack closure. Also, the mutliphase synergistic strengthening mechanism which occurs under cyclic deformation is evaluated.

CP01.04.07
Photocatalytic Disinfection Using GO/TiO2 Nanocomposite Against Escherichia coli and Study on Effect of Reactive Oxygen Species (ROS) Christeena T. Thomas, Myriam Solis López, Roberto Hernández, Martha Barajas Aceves, Jose Tapia Ramirez, José Álvaro Chávez Carvayr, Antonieta García Murillo, Felipe de Jesús Carrillo, Eleicer Ching, and S. Velumani. 1, 2, 4CIVESTAV-IPN, Mexico City, Mexico; 3Programa en Nanociencias y Nanotecnología, Centro de Investigación y de Estudios Avanzados del IPN, Mexico City, Mexico; 4Genética y Biología Molecular, Centro de Investigación y de Estudios Avanzados del IPN, Mexico City, Mexico; 5Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico City, Mexico; 6Ingeniero Químico Industrial, Escuela Superior de Ingeniería Química e Industrias Extractivas – IPN, Mexico City, Mexico; 7Departamento de Ciencias Naturales, Universidad Tecnológica de Panamá, Panamá, Panamá; 8IEECS, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico City, Mexico.

Photocatalytic disinfection of Escherichia coli K12 was experimented with the synthesized Graphene oxide/ Titania (GO/TiO2) semiconducting nanocomposites. GO was functionalized with TiO2 to increase efficiency in the disinfection process. Characterizations by scanning electron microscope (SEM) and transmission electron microscopy (TEM) for the surface morphology and Ray diffraction (XRD) for the crystal structure, Raman spectroscopy for the structural Analysis and UV-Vis diffuse reflectance (DR) to determine the band gap in GO/TiO2; semiconducting nanocomposites were carried out. The photocatalytic disinfection was performed under visible light irradiation using a solar simulator. For the study of reactive oxygen species (ROS) in the photocatalytic disinfection of Escherichia coli K12, scavenger study was done. From the XRD results, partial reduction of GO to reduced GO was observed due to the increase in the concentration of GO. The SEM analysis shows the homogeneous distribution of TiO2 nanoparticles over GO. According to Raman results, the corresponding D and G bands were identified at 1342 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively showing the crystalline quality of the synthesized nanocomposites. All these characteristic techniques reveal the enhancement of photocatalytic disinfection by embedding TiO2 nanoparticles in GO. As a result, the electron – hole pair recombination rate was reduced, and photocatalytic inactivation efficiency was increased. ROS, which is responsible for disinfection was identified.

CP01.04.08
Graphene Reinforced Metallic Foam Through Electrochemical Co-Deposition Rui Dai and Qiong Nian; Arizona State University, Tempe, Arizona, United States.

Monolayer Graphene with extraordinary mechanical properties and super large specific surface area arouses extensive scientific interests as the potential reinforcement for fabrication of lightweight, high strength and stiffness metal-matrix composites. Previous experimental studies have demonstrated this reinforcement effect of graphene in a variety of metal matrix composites mainly in the shape of thin film or thick bulk, however, few talked about its reinforcement efficiency in the three-dimensional (3D) structure. Herein, to reveal the reinforcement effect of graphene in the 3D structure, a graphene-nickel composite foam has been fabricated through applying electrochemical co-deposition process. Specifically, a Polyurethane (PU) foam with the stochastic lattice structure is selected as the template, on which the graphene nano-foam and nickel matrix were co-deposited through adjusting the electrochemical deposition conditions. Afterwards, the PU template was removed by a thermal decomposition process and the lightweight nickel foam in consist of hierarchy open cells and hollow triangle ligaments was obtained. Computational simulations and theoretical modeling were utilized to understand the underlying mechanisms and provide a comparison to the experimental results. Our study on the 3D graphene-metal composite foam sheds light on fabricating novel high strength mechanical metamaterial.

CP01.04.09
Sintering Behavior in Thin Film of Ni Nanoparticle through In Situ Stress Analysis for MLCC Internal Electrode Mingjeong Choi, Wonhyo Joo, Cheol Kim, Kyungryul Lee and Young-Chang Joo; Seoul National University, Seoul, Korea (the Republic of).

Recently, the trend of miniaturization of electronic components is accelerated due to the spread of mobile devices. In particular, Multi-Layer Ceramic Capacitor (MLCC), made by stacking Ni paste layers and ceramic slurry layers alternately followed by a high-temperature sintering process, has a layer thickness of less than 1 μm. One of the biggest issue in MLCC is difference in sintering behavior between ceramic and metal layer and subsequent twisting or fracture due to that. In order to identify the origin of such problem and reduce it, a quantitative tool for analyzing the sintering behavior of the thin film form is required. However, at present, the analysis of sintering behavior of μm scale thin films is limited to indirect methods such as ex-situ microstructure change analysis. In this study, the sintering behaviors in thin film of Ni nanoparticle were successfully analyzed by measuring the stress variation of thin films using laser based optical analysis. First, a Ni paste of 80nm particles was applied evenly on a ceramic substrate by spin coating and it was heated up to 580°C in a chamber filled with N\(_2\) gas mixed with H\(_2\) gas for preventing oxidation. In this process, the stress curve versus temperature with 4 inflection points was obtained. Among them, the points related to the evaporation and decomposition of the solvents in the paste were excluded by comparison with the TGA data, and only one inflection point near 430°C remained. Then the microstructural analysis was carried out for the samples quenched at the temperatures below and above the point. Finally, it was found that the inflection point has a significant relation with the neck formation in the sintering process. The same results were obtained for Ni-alloy materials. This study suggests a method of in-situ analysis of the sintering behavior of metal nanoparticles through stress analysis, and it is expected to act as useful guide line for the study of materials requiring high-temperature sintering process.

CP01.04.11
In Situ Mechanical and Electromechanical Testing of Piezoresistive Nanowires During Scanning Electron Microscopy Sijia Ran and Steven T. Boles; The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

The fundamental relationship between electronic transport properties and applied strain in piezoresistive materials permits their usage in a broad range of applications related to electromechanical systems. Furthermore, strain engineering has been demonstrated as a useful technique to improve the performance of electronic devices, as it allows for enhanced carrier mobility and direct control of the band gap of semiconductors. Quantitative characterization of the relationship between electrical properties and strain is essential to the development of piezoresistive-based devices and to the application of strain-engineered devices. To quantify fundamental piezoresistive properties and reach high strain levels, testing at the nanoscale is critical, as the size scales can fall below the threshold for external or bulk defects. However, proper characterization of the piezoresistivity is a challenge at the nanoscale due to the miniscule specimen size. In this work, in situ tensile tests inside a scanning electron microscope (SEM) are conducted to study the mechanical and electromechanical properties of tellurium (Te) and germanium (Ge) nanowires. The in situ tensile testing technique allows real-time observations of elastic/plastic behaviors and gives the resistance changes under different strains for the determination of the piezoresistivity. The reversibility and the repeatability of the observed piezoresistive properties can be confirmed from loading-unloading tests and measurements of multiple nanowires with different diameters. These tests offer accurate experimental data that yields insights into the fundamental mechanisms behind piezoresistivity, such as strain-induced changes in band structure.

CP01.04.12
Piezoelectric Response of Sn-Doped BaTiO\(_3\) Epitaxial Thin Film TaeYeon Kim, 1 Sanjith Unithrattil, 2 Jun Young Lee 1 and Su Yong Lee 1; 1Gwangju Institute of Science and Technology, Seoul, Korea (the Republic of); 2Pohang Accelerator Laboratory, Pohang, Korea (the Republic of).

Accompanying with doping of Ca, Zr, etc, BaTiO\(_3\)-based ceramics exhibited excellent dielectric behaviors. Especially, Sn has been found to increase the permittivity by 3 times in comparison with single BaTiO\(_3\) and to induce the relaxor-type behavior.1,2 Recent transmission electron microscopy studies3 have shown that polar nano region (PNRs) embedded in the matrix is responsible of relaxor behaviors. The lattice constant increases with the doping of Sn, and the PNR region expands due to the stress of the matrix which has a large effect on the ferroelectricity of materials. Through high-resolution scanning transmission electron microscopy and first order calculation[4], they confirm the unit cells of the PNRs expand by the stress, which indicates that there is more space between Ti atoms and the oxygen octahedra to allow larger off centre displacements. This result shows an extreme improvement in dielectric permittivity. In addition, experimental methods of applying the temperature and electric field to control the stress in the PNR region have been proposed, and simulation has confirmed that these elements increase the piezoelectricity of the relaxor ferroelectric materials.[5,6] However, the relationship between PNR and electric field of the Ba\(_{(1-x)}\)Sn\(_{x}\)TiO\(_3\) (BTS) film was not confirmed experimentally. Therefore, we use a combination of time-resolved micro-X-ray diffraction (TRXD), which is used to apply biaxial stress to the thin film in real time. As a results, we confirm the relationship between PNR with piezoelectric response through calculation of the correlation length in Ba\(_{(1-x)}\)Sn\(_{x}\)TiO\(_3\) (BTS) film.
Shear Banding and Fracture Behavior in Bulk Metallic Glasses Under Quasi-Static and Dynamic Shearing.

The (111)-oriented Nb:Si:TiO thin crystal substrates with a Nb concentration of 0.5% were used as substrates to grow the epitaxial Ba(Ti0.5Sn0.15)O3 thin films on top. The BaTiO3 film was deposited using pulsed laser deposition (PLD) in an oxygen atmosphere of 10 mTorr. After the deposition, the samples were cooled down in a high vacuum. The dielectric constant was 412, which is twice as high as that of the conventional BTO (about 200). In Pohang Light Source, an X-ray beam with energy of 8 keV was focused to a spot with a size of 11.5 μm onto a circular Pt top electrode with a diameter of 100 μm. With an application of electric field (364 MV/m), (111) reflections of film shifted to the lower q, value from 2.696 to 2.691 Å, which indicates the piezoelastic expansion with piezoelectric coefficient of 6.7 pm/V. We deposited the BTO thin film through PLD for the first time, and experimentally observed the piezoelectric properties as an electric field was applied. The change in the PNR region was confirmed from the results.

In the recent years, replacing the current Zr-alloy-based cladding with silicon carbide composites has gained traction in the Department of Energy (DOE) as well as in the industry. The most recent generation of SiC/SiC composites (III), defined by near-stoichiometric chemical composition and crystallinity with reduced oxygen content, has been extensively tested for nuclear applications. They are comprised of a SiC matrix (m) reinforced with long SiC fibers (f) that are woven or braided onto a tubular cladding configuration. The properties of SiC/SiC composites are greatly influenced by the matrix processing methods, fiber architecture and orientation, and interface materials. Oxidation reaction kinetics under steam attack is of critical importance under accident conditions. When exposed to steam, SiC exothermically forms silica, hydrogen and carbon monoxide releasing an energy of 223 kJ/mol, approximately. In general, a competition between a parabolic oxidation process and a linear volatilization process results in paralinear kinetics.

In this work, we capture the oxidation process in a model composite material using a combination of x-ray tomography and mesoscale phase-field simulations. First, the microstructure of the composites is faithfully extracted by x-ray tomography and a full three-dimensional reconstruction is performed. This nondestructive technique allows us to extract all the pertinent microstructural details. Starting with the digitized microstructure, we then simulate the evolution of the pores/pathways accompanying the transport of steam through phase-field modeling. Non-equilibrium chemical thermodynamic models are used to make accurate predictions on the pertinent chemical reactions. The evolution equations (Allen–Cahn and Cahn-Hilliard), which are fully coupled to heat conduction and deformation models, allow us to determine the extent of oxidation processes in the composites under anticipated accident conditions.

In Situ Growth of Nanodefects in Si

Nucleation and growth of oxygen precipitates in Czochralski Si crystals with different boron dopings has been investigated in-situ up to 1000°C to monitor their structural evolution from the very early stages to a stable configuration. Thickness-dependent Pendellosung oscillations as described by the dynamical theory of X-ray diffraction are extremely sensitive to strain fields from defects in a host crystal. Based on this, we initiated a novel approach to study the precipitation kinetics of oxygen in Si. A diffusion-limited model of growing spherical precipitates with two growth regimes interprets the data. An initial diffusion-driven progression is followed by a long time precipitation behavior, which is interpreted as Ostwald ripening.

Large Dielectric Constant Enhancement in MXene Percolative Polymer Composites

We demonstrate that poly(vinylidene fluoride) (PVDF)-based percolative composites using two-dimensional (2D) MXene nanosheets as fillers exhibit significantly enhanced dielectric permittivity. The poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) (PVDF-TrFE-CFE) polymer embedded with 2D Ti,C,T nanosheets reaches a dielectric permittivity as high as 10 near the percolation limit of about 15 wt % MXene loading, which surpasses all previously reported composites made of carbon-based fillers in the same polymer. Up to 10 wt % MXene loading, the dielectric loss of the MXene/PVDF-TrFE-CFE composite indicates only an approximately fivefold increase (from 0.06 to 0.35), while the dielectric constant increased by 25% times over the same composition range. Furthermore, the ratio of permittivity to loss factor of the MXene-polymer composite is superior to that of all previously reported fillers in this same polymer. The dielectric constant enhancement effect is demonstrated to exist in other polymers as well when loaded with MXene. We show that the dielectric constant enhancement is largely due to the charge accumulation caused by the formation of microscopic dipoles at the surfaces between the MXene sheets and the polymer matrix under external applied electric field.

Thermal Conductivity of 3D Graphene Reinforced Cu Composite Fabricated by a Simple Two-Step Process

Cu composite reinforced by three-dimensional (3D) graphene network was synthesized in a simple two-step process; (1) an axial compaction of Cu particles in a mold, and (2) CVD at an appropriate condition leading to a Cu composite reinforced with 3D graphene network. Cu composites with different contents of either graphite or graphene were obtained by controlling the processing parameters. 3D graphene network reinforced Cu composite is presented with a possible explanation for and characterization of the formation of graphene. Lastly, the thermal conductivity data of 3D graphene-Cu composite, which is currently about 450 W/mK in both perpendicular and parallel directions, is presented along with a possible mechanism to explain the high thermal conductivity.
8:00 AM *CP01.05.01
Deformation and Failure Behavior of 3D Micro-Architected Lattice Materials
Wei Huang, Mark Wong, Arturo Mateos, Julia Greer and Yong-Wei Zhang; 1School of Aeronautics, Northwestern Polytechnical University, Xi'an, China; 2Institute of High Performance Computing, A*STAR, Singapore, Singapore; 3Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California, United States.

3D micro-architected structural meta-materials are instrumental in light-weight, high-strength, and damage-tolerance engineering applications. The reliability of such materials is often dictated by the mechanical properties of their truss components such as nanowires and nanopipes and their defects, such as notches and voids and also structure-level defects that disrupt the connection of the lattices. An in-depth understanding on the effects of component-level factors such as grain boundaries, surface roughness, sizes, shapes and man-made notches and structure-level factors such as the sizes and shapes of the connection disruptions on the deformation mechanisms and failure patterns of 3D micro-architected meta-materials is of great importance to their fabrication and services with high reliability. In this talk, we will first report our recent progresses in the study of the effects of component-level factors such as grain boundaries, surface roughness, and the sizes, shapes and man-made notches on the plasticity and failure of the components using both computer simulations and mechanical testing. We will then report our recent work on the effect of temperature and component size on the deformation and failure of micro-architected meta-materials under compression and tension using both computer simulations and mechanical testing. Finally, we discuss the effect of structure-level defects (connection disruption) on the failure behavior of 3D micro-architected meta-materials under tension using both finite element modeling and mechanical testing. The present works explore the size effect, temperature and flaw sensitivity of 3D nanolattices and their components using both simulations and experiments, and demonstrates various interesting and unique features of the architected structural meta-materials.

8:30 AM *CP01.05.02
Systematic Study of Electron-Beam Assisted Plasticity for Amorphous Silica Nanostructures
Sung-gyu Kang, Woonjin Cho, Heung Nam Han and In-Suk Choi; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

In this study, we explore the effect of electron-beam irradiation on the mechanical behavior of amorphous silica nanostructures. It has been reported that amorphous silica exhibits ductile deformation behavior under the electron-beam irradiation during the in-situ compression testing. However, the dependency of electron-beam conditions such as acceleration voltages and beam currents has not been thoroughly investigated. Hence, we performed in-situ mechanical testing for amorphous silica nanostructures at various electron-beam conditions. By systematically changing acceleration voltages and electron-beam currents, we found the threshold electron-beam condition to induce plastic deformation of amorphous silica. Furthermore, our simulation study suggests that the electron-beam effect has clear correlation with the interaction volume of the electron-beam with the sample.

9:00 AM CP01.05.03
3D Printing and Mechanical Testing of Polymer-Graphene Composite Lattices
Kalaimani Markandan; Nanyang Technological University, Singapore, Singapore; 
Wei Huang, Mehrdad Kiani, Yifan Wang, Nicolas Bertin and Wei Cai; Stanford University, Stanford, California, United States.

3D printing has become a popular fabrication technique for rapid prototyping of complex structures in recent years due to its simplicity, relatively short production time and low material wastage. Despite these advantages, it remains difficult to fabricate structures out of composite materials, such as nanofiller-reinforced polymer resins, using 3D printing. Here, we investigate the factors influencing the stereolithographic synthesis of 3D structures, such as concentration of filler and post-fabrication baking temperature and duration, and demonstrated, for the first time, the successful fabricate graphene-polymer composite lattices. Quasistatic mechanical tests showed that the stiffness of a polymer, reinforced with as little as 0.02 wt. % graphene, can increase up to 70.2 % compared to a non-reinforced polymer. Furthermore, enhanced energy absorption was also observed for octet-truss lattices 3D printed from the polymer-graphene composite material. In situ microscopic deformation and failure of the 3D printed graphene-polymer composite during mechanical testing will be presented and discussed as well.

9:15 AM CP01.05.04
Strengthening Mechanisms in Bimetallic Core-Shell Nanocubes
Wendy Gu, Mehrdad Kiani, Yifan Wang, Nicolas Bertin and Wei Cai; Stanford University, Stanford, California, United States.

Strength, ductility and toughness are key attributes of precipitate strengthened alloys, but remain challenging to achieve in many metallic systems. A detailed understanding of dislocation dynamics at precipitates is necessary for controlling work hardening, localized plasticity, plastic reversibility (e.g. Bauschinger effect), fatigue and failure, as well as the development of high performance steels, lightweight alloys, and high-temperature superalloys. Progress in these areas has been hampered by the lack of direct experimental evidence of detailed deformation mechanisms at precipitates, which prevents the verification and calibration of physics-based predictive computational models. Here, we use bimetallic core-shell nanocubes as model systems in which single precipitates (core nanocrystal) are isolated, and colloidal chemistry is used to tailor precipitate size, composition and defect structure. Nanocrystals are compressed using in-situ scanning electron microscope to obtain stress-strain behavior at individual precipitates, and characterized before and after compression using transmission electron microscopy. Molecular dynamics and discrete dislocation dynamics simulations are compared to experiments in order to determine the dislocation mechanisms responsible for the mechanical response. Here, we compare the mechanical behavior at semi-coherent precipitates in Au@Cu core-shell nanocubes and coherent precipitates in Au@Ag nanocubes. Au@Ag nanocubes have misfit dislocations at the core-shell interface and threading dislocations within the Cu shell, while Au@Cu nanocubes are defect-free. Au@Cu core-shell nanocubes are found to have higher strength, and strain hardening that is absent in Ag and Au@Ag nanocubes. We determine that deformation in Au@Cu nanocubes is governed by the motion of threading dislocations that extend from the bimetallic interface to the nanocube surface, that operate as single-arm sources. Plastic deformation in Au@Ag nanocubes occurs through the nucleation of dislocations at free surfaces.

9:30 AM BREAK

10:00 AM *CP01.06.01
Plasticity and Fracture in Metallic Materials with Hierarchical Nano/Microstructures
Amit Misra; University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

This presentation will review the recent progress in the understanding of plastic deformation and fracture in metallic materials that have hierarchical composite structures across nano-to-micro length scales. Examples will be presented from different model systems such as laser-processed Al-Al2CuSi eutectics, and vapor deposited Cu-Mo thin films. The role of in situ straining experiments in TEM and SEM, and integration with atomistic modeling, dislocation theory and crystal plasticity in understanding mechanical behavior will be emphasized. The common aspects in interface-dominated mechanical behavior in hierarchical metallic composites such as unusually high flow strengths, high strain hardening rates, plastic co-deformability and suppression of shear bands will be highlighted.

10:30 AM *CP01.06.02
Indentation and Helium Implantation Response of TaTi/ZrTi Nanocomposites Fabricated Via Solid Metal Dealloying Michael Demkowicz; Texas A&M University, College Station, Texas, United States.

We use solid metal dealloying to synthesize TaTi/ZrTi nanocomposite thin films with widely differing morphologies of the constituent phases, ranging from particulate to bicontinuously interpenetrating, but comparable characteristic dimensions of microstructure features. We then investigate the indentation and helium implantation response of these composites. Our work shows a systematic dependence of indentation pile-up height on microstructure morphology, which we attribute to morphology-induced differences in strain hardening rates. We also find a reduction in the size and distribution of helium precipitates relative to un-dealloyed materials, which we relate to the characteristic dimensions of microstructure features of the composites. We conclude with a discussion of future prospects for tailoring mechanical and radiation response by changing microstructure morphology in dealloyed composites.

11:00 AM CP01.06.03 Unraveling the Material and Microstructural Features Prompting Sub-Crystalline Localization in Polycrystalline Ni-Based Superalloys Marat Latypov1, Jean-Charles Stinville2, Jason Mayeur2, Tresa Pollock1 and Irene J. Beyerlein1; 1University of California, Santa Barbara, Santa Barbara, California, United States; 2The University of Alabama in Huntsville, Huntsville, Alabama, United States.

Annealing twins can have a strong impact on the mechanical performance of Ni-base superalloys used in turbine disks. While they are recognized for helping to increase yield strength, annealing twins are also known to localize strain and initiate microcracks in high-cycle fatigue. Using a combination of in-situ deformation DIC and 3D crystal plasticity based computational modeling, we investigate the microstructural factors leading to strain localization and subsequent slip band initiation. The analysis focuses on the coupled role of elastic anisotropy, grain neighborhoods, and grain shape and size in determining the location of the exceptionally preferred points of high elastic strain concentration and localized slip, when the applied strain is under but near the macroscopic elastic-plastic transition. We find that the very few localized slip bands are correlated to the development of only the highest elastic strain concentrations. The latter develops in grains that have an outstandingly compliant orientation relative to its neighbors. We discuss some important microstructural features responsible for microcrack initiation as revealed by the model calculations.

11:30 AM CP01.06.04 An Analysis of the Deformation and Fracture Mechanisms of Cu/Nb Nanolaminates by In Situ TEM Mechanical Tests Javier Llorea, Zhihui Liu, Miguel A. Monclus, L. W. Yang, Miguel Castillo-Rodriguez and J. M. Molina-Aldareguía; IMDEA Materials Institute, Getafe, Madrid, Spain.

Nanoscale metallic multilayers formed by alternating layers of two dissimilar metals with layer thicknesses in the nanoscale range have very attractive properties including high hardness, strength and thermal stability. Nevertheless, most of the mechanical characterization of metallic nanolaminates has been carried out by means of nanoindentation or micropillar compression and very little information is available on the tensile behaviour of free-standing nanolaminates films. Thus, there is a lack of information on the deformation and fracture mechanisms of these systems in tension. In this investigation, the mechanical behaviour of Cu/Nb nanolaminates manufactured by accumulated roll bonding were studied by means of tensile tests carried out within a transmission electron microscope (TEM). Tensile specimens with the loading axis parallel and perpendicular to the laminate were milled using a focus ion beam gun and attached to a push-pull loading device which was introduced in the TEM. Load and deformation were recorded during the in situ tensile deformation, together with the mechanisms of deformation, crack propagation and crack arrest at the Cu/Nb interfaces. Evidence of plastic deformation by confined layer slip was found in both orientations for Cu and Nb, but important differences were found in the fracture mechanisms between both orientations. Crack nucleation and propagation was localized in the thickest Cu layer when the nanolaminates was perpendicular to the loading axis. In the parallel orientation, crack was nucleated in a Cu layer but was stopped at the Cu/Nb interface, leading to a rough crack path. The influence of the orientation on the deformation and fracture mechanisms was discussed to the light of the observations provided by the in situ mechanical tests.

11:45 AM CP01.06.05 In Situ TEM on Twinning Plasticity in Nano-Sized HCP Metals Scott X. Mao1, Yang He1 and Chongmin N. Wang2; 1University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 2Pacific Northwest National Laboratory, Richland, Washington, United States.

Twinning is an essential carrier of plastic deformation and critically influences the mechanical behavior of materials. Due to its atomic-scale complexity, the atomic mechanism of twinning nucleation and growth in hexagonal close-packed (HCP) crystals remains theoretical contention to date, which largely impedes the design and processing of high strength alloys. Here, by using in situ transmission electron microscopy, twinning mechanism was directly captured in HCP crystals. In stark contrast to the classical twinning dislocation mechanism, it was found that {1 0 -1 2} twinning nucleation could be dominated by atomic shuffles which were manifested by the direct transformations between prismatic and basal planes; this process established the lattice correspondence of the {1 0 -1 2} twin. During the twin growth, the incoherent B│P-type twin boundaries transformed to coherent twin boundaries which propagated by the movement of classical twinning disconnections. The findings resolve long-standing controversies in twinning of HCP crystals, opened the way for twinning-based design and processing of high strength HCP alloys, and hold broad implication to the deformation in complex crystal structures.

SESSON CP01.07: Xtreme Materials Design—Nanolayers II Session Chairs: Irene Beyerlein, Arief Budiman, Michael Demkowicz and Jessica Krogstad Wednesday Afternoon, April 24, 2019 PCC West, 100 Level, Room 101 A

1:30 PM *CP01.07.01 Strength, Plasticity and Irradiation Properties of Amorphous Ceramics Containing Nano-Sized Metal Additions Jian Wang, Kaisheng Ming, Qing Su and Michael Nastasi; University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

Radiation induced damage in the core structural materials that are made of crystalline materials are microstructural/crystal defects. Conceptually, these defects can be visualized as regions where there is either a deficiency of lattice atoms (voids, vacancies, edge dislocations, vacancy type dislocation loops) or an excess of lattice atoms (self interstitial atoms, interstitial type dislocation loops). All these defects lead to changes in the mechanical properties of the material. For example, radiation induced swelling (by vacancies and voids) causes dimensional distortion and embrittlement, and is a life-limiting materials issue for structural materials in nuclear power reactors. Austenitic steels were used in fast reactors but could not reliably serve beyond ~150 dpa. Ferritic and ferrite-martensitic (FM) steels have been found to swell much less than austenitic steels. Nano-structuring of both austenitic and FM steels appears to be a promising avenue for further improvement of swelling resistance, providing such structures are stable under ion irradiation. Advanced oxide dispersion strengthened alloys were found to be a promising core structural material, but amorphization and dissolution of oxide particles under high dpa irradiation challenges potential applications. Interfaces (interphase boundaries and grain boundaries) between the metal matrix and nanoscale oxides in oxide dispersion strengthened (ODS) steels systems prove to benefit swelling resistance and creep stiffness. Nanoscale metallic interfaces have shown strong defect sink strength and the ability to suppress He bubble formation. However, all of these do not change the intrinsic issue — radiation induced damage in crystalline materials. Compared to crystalline solids, amorphous materials possess no translational symmetry, and amorphous materials do not contain conventional crystal defects such as vacancies, interstitials, or dislocations.

There are two unique radiation effects which must be considered for the irradiation response of amorphous materials: thermal spike formation associated with damage cascades. Our work shows a systematic dependence of indentation pile-up height on microstructure morphology, which we attribute to morphology-induced differences in strain hardening rates. We also find a reduction in the size and distribution of helium precipitates relative to un-dealloyed materials, which we relate to the characteristic dimensions of microstructure features of the composites. We conclude with a discussion of future prospects for tailoring mechanical and radiation response by changing microstructure morphology in dealloyed composites.

2:00 PM *CP01.07.02 Radiation induced damage in the core structural materials that are made of crystalline materials are microstructural/crystal defects. Conceptually, these defects can be visualized as regions where there is either a deficiency of lattice atoms (voids, vacancies, edge dislocations, vacancy type dislocation loops) or an excess of lattice atoms (self interstitial atoms, interstitial type dislocation loops). All these defects lead to changes in the mechanical properties of the material. For example, radiation induced swelling (by vacancies and voids) causes dimensional distortion and embrittlement, and is a life-limiting materials issue for structural materials in nuclear power reactors. Austenitic steels were used in fast reactors but could not reliably serve beyond ~150 dpa. Ferritic and ferrite-martensitic (FM) steels have been found to swell much less than austenitic steels. Nano-structuring of both austenitic and FM steels appears to be a promising avenue for further improvement of swelling resistance, providing such structures are stable under ion irradiation. Advanced oxide dispersion strengthened alloys were found to be a promising core structural material, but amorphization and dissolution of oxide particles under high dpa irradiation challenges potential applications. Interfaces (interphase boundaries and grain boundaries) between the metal matrix and nanoscale oxides in oxide dispersion strengthened (ODS) steels systems prove to benefit swelling resistance and creep stiffness. Nanoscale metallic interfaces have shown strong defect sink strength and the ability to suppress He bubble formation. However, all of these do not change the intrinsic issue — radiation induced damage in crystalline materials. Compared to crystalline solids, amorphous materials possess no translational symmetry, and amorphous materials do not contain conventional crystal defects such as vacancies, interstitials, or dislocations.

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The Influence of 3D Interfacial Structure and Morphology on the Mechanical Behavior of Nanocomposites

Nathan Mar|1, Youxing Chen|1, Kevin Schmalbach|1, Justin Cheng|2, Zhao Wang|2, Nan Li|1, Jon Kevin Baldwin|2, David Poerschke|1, R. Lee Penn|1 and Andreas Stein|1

1University of Minnesota, Twin Cities, St. Paul, Minnesota, United States;
2Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Two-dimensional (2D) sharp interfaces with distinct boundaries demarcating an abrupt discontinuity in material properties in nanolayered composites have been studied for almost twenty years and are responsible for enhanced behaviors such as strength, radiation damage tolerance, and deformability. However, 2-D interfaces have their limitations with respect to deformability and toughness. 3D interfaces are defined as heterophase interfaces that extend out of plane into the two crystals on either side and are chemically, crystallographically, and/or topologically divergent, in three dimensions, from both crystals they join. Here, we present the mechanical behavior of three different classes of nanocomposites:

1) nanolayered Cu/Nb containing interfaces with 3D character and 2) Tungsten-based 3D ordered nano/mesoporous composites consisting of a porous W scaffolding with silicon carbide or silicon nitride infill. Micropillar compression results show that the strength of Cu/Nb nanocomposites containing 3D interfaces is significantly greater than those containing 2D interfaces. Shear banding in 3D Cu/Nb is observed during pillar compression with retention of continuous layers across the shear band. We will present our recent results on deformation of such 3-D interfaces and structures, and describe this evolution mechanistically through the use of atomistic simulations.

2:30 PM BREAK

3:30 PM *CP01.07.03

Cyclic Plasticity and Damage Behavior of Metals at the Nanoscales

Xue-Mei Lau|1, Hong-Lei Chen|2, Li-Xue Zheng|1 and Guang-Ping Zhang|1

1Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; 2School of Materials Science and Engineering, University of Science and Technology of China, Shenyang, China.

Fatigue of metals at the nanoscales has drawn extensive attention due to not only the long-term service reliability of nanoscale metallic components in micro/nano-devices, but also the fundamental understanding of the mechanical fatigue mechanisms at the materials at the nanoscales. It has been demonstrated that the decrease in the length scale from micron scales to submicron scales strongly constrains the formation of typical dislocation structures (dislocation walls and cells), and thus suppresses cyclic strain localization, leading to the enhancement of fatigue strength. In this talk, we will present ex-situ TEM investigations on cyclic plasticity and damage behavior of metals at the nanoscales, such as nanocrystalline metal films and metallic multilayers. For nanocrystalline metal films with a thickness ranging from 20 to 930 nm, we found an evident transition of cyclic plasticity from full dislocation-dominated to partial dislocation-controlled behavior, meanwhile grain boundaries exhibit the unstable behavior related to the film thickness. Furthermore, the fatigue damage behavior was characterized, and slip irreversibility was estimated theoretically based on the observations of dislocation activities. For the nanoscale metallic multilayers, we found that the heterogeneous layer interface in the Cu/Ta multilayers with different layer thicknesses exhibits different stability under cyclic loading. The fatigue damage mechanism and the scaling effect on the slip irreversibility, grain boundary as well as heterogeneous layer interface instability of the metal films and multilayers at the nanoscales will be discussed.

4:00 PM *CP01.07.04

Advances in In Situ Microfracture Experimentation Techniques—Enabling Enhanced Fracture Properties of Cu/Nb Nanolayers via Interface Interaction Engineering

Hashina Parveen Anwar Ali|1, Nan Li|2 and Arief S. Budiman|1

1Xtreme Materials Laboratory, Engineering Product Development (EPD), Singapore University of Technology and Design (SUFTD), Singapore, Singapore; 2Center for Integrated Nanotechnologies (CINT), Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Plasticity and fracture of materials at the nanoscales can deviate significantly from the same phenomena in bulk properties, which may have important implications if the materials are to be used in real-world engineering systems. Nanoscale metal-metal multilayered materials, where interfaces can be created and modulated in a highly controlled manner and with relative ease, provide a model material system platform to understand plasticity and fracture based on their interactions with other microstructural features at the nanoscales. Recently, there is a growing trend to understand fracture of multilayered materials to see the interactions between the crack and multilayered interface through novel experimentation techniques. In this review, we will introduce the rationale behind this trend and the current microfracture testing methods to test and analyze multilayer fracture behavior. Four examples of in situ fracture techniques are highlighted in this work – the in situ observation upon tensile testing of film on a substrate, the in situ microfracture clamped beam bending technique across the multilayers for accumulative roll bonded as well as physical vapor deposited multilayers and the in situ delamination of metal-metal multilayers along the multilayered interface.

SESSION CP01.08: Advances in Xtreme Experimentation—Synchrontron Micro XRD I

Session Chairs: Arief Budiman and Olivier Thomas

Thursday Morning, April 25, 2019

PCC West, 100 Level, Room 101 A

8:00 AM *CP01.08.01

Advanced In Situ X-Ray Diffraction Strategies for the Evaluation of Structure, Strains and Defects in Functional Materials

Olivier Thomas|1,2,3

1Aix Marseille Universite, Marseille, France; 2Université de Toulon, Toulon, France; 3IM2NP, CNRS, Marseille, France.

In present synchrotron radiation facilities, the trend towards fast on-the-fly experiments [1,2], made possible in particular thanks to faster low noise hybrid pixel area detectors, opens many avenues for in situ evaluation of structure, strain and defects in various nano-materials. Pole figure measurements can now be performed fast enough to follow intriguing texture changes during phase transformations [3]. Combination of curvature measurement with x-ray diffraction allows for a detailed understanding of strain evolution during crystallization of phase change materials [4]. Thanks to focused beams strain mapping in devices can be performed in situ as a function of temperature [5]. I will also show how small x-ray beams may be used for investigating the mechanical behavior of nano-objects in situ during mechanical testing [6,7]. All these recent evolutions will benefit a lot from the development of new and even more brilliant sources which will appear in the coming years.


8:30 AM CP01.08.02

In Situ Study on the Strain Partitioning in a Duplex Stainless Steel by Synchrontron X-Ray Diffraction, SEM, µ-DIC and EBSD

Xiao Zhang|1,2, Pei Wang|1, Dianzhong Cheng|1, Nan Li|2, Si-Xue Zheng|1 and Guang-Ping Zhang|1

1Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; 2School of Materials Science and Engineering, University of Science and Technology of China, Shenyang, China.

Advanced
The strain partitioning between austenite and ferrite, and grain rotation in a duplex stainless steel are studied in situ during uniaxial tensile loading by a method combining synchrotron X-ray diffraction with SEM, μ-DIC and EBSD. The multi scale results show that at the elastic stage, austenite strain partitioning happens. As the sample comes into the plastic stage, when austenite deforms plastically and ferrite deforms elastically, strain partitioning between phases and grains with different orientations happens. At this time austenite undertakes more strain, and strain accumulates within austenite grains around the phase boundaries and grain boundaries. As the applied stress increases further, both austenite and ferrite strain partitioning plastically. Strain accumulates within the entire austenite grains and ferrite grains around the phase boundaries. Strain gradient exists in both austenite grains and ferrite grains which causes significantly grain rotation at this stage. The research makes up for the disadvantage of the synchrotron X-ray diffraction by applied in the in situ SEM, μ-DIC and EBSD, which gives a new sight on the studying of the micro deformation of multi-phase materials.

8:45 AM *CP01.08.03
In Situ Full Field Diffraction X-Ray Imaging of Buried Tilt and Strain Fields in Light Ion-Implanted Si Wafers Antoine Peulin,1 Samuel Tardif2, Tao Zhou3, Frédéric Mazen3, Joël Eymery4 and François Rieutord2; CEA-LETI, Grenoble, France; 2CEA-INAC, Grenoble, France; 3ESRF- The European Synchrotron, Grenoble, France.

The Smart CuTM technology, which is based on the implantation of light ions in a crystalline matrix, is well-suited for the production of Silicon-On-Insulator (SOI) substrates used in electronics. Under annealing the gas implanted in the crystal forms defects that evolve into micro-cracks, which eventually leads to a subsurface fracture and the delamination of a thin crystalline layer. Bonding the implanted crystal to an oxidized substrate prior to the splitting, allows one to obtain a SOI substrate with a nanometer-thick top silicon layer.

However, the physics leading to delamination is still not fully understood and it is difficult to selectively measure the brittle, implanted layer when a wafer is bonded on top. The aim of this study was to find a way to measure in situ the effect of these buried micro-cracks in terms of lattice strain and tilt on the crystalline matrix under annealing.

A new method called Full Field Diffraction X-ray Microscopy (FFDXM) has been used to observe the deformation induced by the gas-filled micro-cavities in the Smart CuTM technology. This method has been developed at the European Synchrotron Radiation Facility (ESRF) at the ID01 beamline. It consists in using a well-collimated X-ray beam to diffract on the sample and post-sample lenses to obtain a real space image on a two-dimensional detector of the Bragg reflection, quite similar to dark-field imaging in electron microscopy. It allows direct imaging of crystalline domains with a space resolution of some hundreds of nanometers over hundreds of microns, with possible orientation and/or strain contrast. Using hard X-rays (10 to 20 keV), it is possible to image buried features, e.g. at the interface of two bonded wafers.

The acquisition time of FFDXM (on the order of the minute) is compatible with the annealing times in the Smart CuTM technology (on the order of the hour). Thus it has been used in situ to follow the evolution and the movement of the micro cavities coalescence mechanism and the spatial extent of their tilt/strain fields during annealing, a key point to improve understanding of silicon fracture mechanisms after light ion implantation.

9:00 AM *CP01.08.04
In Situ Nano X-Ray Tomography for High-Resolution Imaging of Cracks in Composites and Integrated Circuits During Mechanical Loading Kristina Kutukova1, Juergen Gluch1, Izabela Zglobicka1, Christoph Sander2, Andre Clausner1 and Ehrenfried Zschech4; 1Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany; 2Bialystok University of Technology, Bialystok, Poland.

The imaging of crack propagation in mechanically stressed bulk samples and thin film stacks with high spatial resolution is essential for the validation of models based on materials physics and chemistry as well as on fracture mechanics, and eventually for the design of advanced materials with tailored mechanical properties. Information about the kinetics of crack evolution is needed for ensuring the in-service mechanical performance and reliability of advanced products. Laboratory X-ray microscopy and nano X-ray computed tomography (nano XCT) offer intrinsic advantages for 3D in-situ imaging of cracks in multi-component materials and structures, since they are nondestructive, i.e. the material itself and the local strain state are not modified by sample preparation. We will present experiments that combine nano XCT and mechanical loading for visualization of crack evolution in composites and in 3D patterned microchip structures.

The combination of nano XCT with micro-mechanical experiments merges the advantages of high-resolution 3D imaging of the microstructure of materials with the observation of phenomena like crack propagation during mechanical loading. The application of in-situ mechanical loading of multi-component materials is demonstrated. A customized micro-mechanical test setup is designed for in-situ nano-indentation experiments in such a way that it fits into the limited space of the nano XCT tool and that the indenter tip and the sample fit into the field of view of the X-ray microscope. Cracks in carbon fibre reinforced aluminum matrix composites along interfaces are imaged using XCT, to evaluate the fracture behavior of MMCs.

A miniaturized double cantilever beam test in an X-ray microscope is used for in-situ imaging of crack evolution in microchips. High-resolution 3D image sequences based on nano XCT are acquired during mechanical loading to visualize crack opening and propagation in on-chip interconnect structures of integrated circuits with about 100 nm resolution [2]. As a result, the weakest layers and interfaces are identified and the robustness of the Cu/low-k interconnect stack against chip-package interaction, a serious reliability concern for microelectronic products, is evaluated. This setup can be used to study the dynamic response of samples during low-cycle fatigue too.

Perspectives to overcome three major limitations of state-of-the-art nano XCT tools, i.e. the need of sample preparation (typically less than 50 mm thickness, depending on the material composition, if 8 keV photons are used), limited space for microelectronic products, is evaluated. This setup can be used to study the dynamic response of samples during low-cycle fatigue too.

This talk will highlight recent advances with in situ Transmission Electron Microscopy (TEM) nanomechanical testing and imaging techniques that provide insight into small-scale plasticity and the evolution of defect structures in materials. With the advent of fast direct electron detectors, it is possible to perform strain mapping during in-situ deformation in a TEM with the precision of a few nanometers using the 4DSTEM technique. This talk will describe our recent results from in situ TEM nanomechanical testing that provide insight...
into multiscale metallurgical phenomena using these techniques, such as the role of short range ordering in Ti alloys and deformation phenomena in metallic glasses.

10:30 AM CP01.09.02
Advances in Nanomechanical Throughput for Extreme Materials Design

Douglas D. Staufner, Eric Hintzula, Ude Hangen and Oden L. Warren; Bruker Nano Surfaces, Eden Prairie, Minnesota, United States.

Advances in materials design often begins with a hypothesis or simulation, and ends with a structure/process/property correlation. In between is synthesis and characterization, often with a very limited sample size necessitated by either the production of a large numbers of samples (e.g. combinatorial studies) or expense (cost of base materials plus synthesis). It is important to get as many structural parameters with that small volume of material as possible, therefore correlative and in situ studies are of primary interest. Here the authors present a nanomechanical testing technique which is capable of very large throughput, capable of collecting more than one million mapped data points on a damascene steel sample in the cm^2 dimensions. The mechanical property map is correlated to both chemical and structural mapping that can be used to generate a full structure/property/process/understanding. This indentation mapping technique can also be compared with in situ microbeam bending tests, for example the transition in a BMG to Ti dissimilar weld from ductile Ti rich, to a ductile BMG with Ti lamella, to fully brittle BMG.

11:00 AM CP01.09.03
Annealing of Metal Films at Room Temperature Using Electron Wind Force and Elastic Strain Energy—An In Situ TEM Study

Zahabul Islam1, Huaqian Gao2 and Aman Haque1; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2Brown University, Providence, Rhode Island, United States.

Grain growth in metallic thin films is commonly achieved with high temperature (greater than 30% of the homologous temperature) annealing. In this study, we explore an alternate route that is non-thermal in nature. Specifically, we study the synergy of electrical current and tensile strain instead of temperature. Our approach involves passing electrical current in the specimens at much lower current density than the electro-migration damage limit. This directly causes Joule heating, which is eliminated by both passive and active heat removal techniques to keep the specimen temperature at or near ambient conditions. We then study the role of mechanical strain on the grain growth at room temperature. In-situ Transmission electron microscopy (TEM) shows more than 10 times grain growth under the application of elastic strain (about 0.1%) dramatically increased the grain size by more than 10 times in a few seconds at the room temperature regions. This suggests that the synergy of elastic strain energy and electrical current density may achieve grain growth in metallic materials even at room temperature. We investigated this phenomenon using molecular dynamics simulation, which reveals that externally applied strain is localized at the grain boundaries in nanocrystalline metals, which promote the effects of electron wind force on the grain boundary atoms. We conclude that synergy of two or more stimuli can achieve grain growth at low or even room temperature.

Our experimental study begins with fabrication of a micro-electro-mechanical system (MEMS) device with 100 nm thick Palladium thin film. Palladium melts at 1555 °C and is used in catalysis and electronics applications. It is therefore an attractive specimen for room temperature annealing. To decouple the contributions from the electrical current, temperature and stress, we developed a unique experimental setup, where the same specimen could be divided into two regions. The center region experiences high temperature and the applied current density. The two edges of the freestanding thin film specimens remain at the same current density, but at around room temperature. The negligible grain growth at the edges suggests the dominant role of temperature on grain boundary mobility. The initially nanocrystalline (5 nm grain size) specimens were exposed to various levels of current density with and without tensile strain inside a TEM. Transmission electron microscope (TEM) images and diffraction patterns show that even elastic strain energy can not only strongly influence the grain growth, but also lower the required electrical current density. The resulting microstructure showed very high density of nano-twins compared to the purely thermally annealed ones.

In addition to the experimental study, we employed classical molecular dynamics (MD) simulation to investigate the underlying mechanism on grain growth using embedded atomic model (EAM) potential. We model the electron flow by imposing an additional equivalent wind force on each atom at room temperature. This equivalent electrical wind force enhances the atomic motion and diffusion at defective regions (grain boundaries), which in turns facilitates the grain growth. The role of mechanical stress is to promote this mechanism through localization at the grain boundaries. Displacement vector analysis of individual grain from molecular dynamics simulation reveals that grain grows due to the grain boundary sliding and rotation during tensile straining accompanied by AC current.

11:15 AM CP01.09.04
In Situ Nanoindentation Tests to Investigate Plastic Deformation and Recovery of Thin 3C-SiC and Change of Mechanical Properties Due to Ion Irradiation

Xuying Liu, Chaiyapat Tangpatjaroen, Izabela Szulifarska and Paul Voyles; University of Wisconsin-Madison, Madison, Wisconsin, United States.

We have used in situ TEM to investigate deformation and failure of 3C-SiC as synthesized and after irradiation with carbon ions. Radiation-induced embrittlement is a significant problem in all kinds of nuclear materials (e.g. [1]). 3C-SiC has shown severe embrittlement and loss of strength under high fluence at relatively low temperature [2]. Our in situ nanoindentation tests on as-synthesized 3C-SiC show that this brittle ceramic can show some plasticity at room temperature. The continuous load-displacement curves confirmed that no fracture happened during indentation, which is also reflected in the TEM videos. Bend contours moved away from the surface during loading, representing the stress field inside the sample under applied force. SEM observation post indentation shows metal-like extrusion around indents, which demonstrates that samples experienced some plastic deformation. In dark-field TEM images after indentation, there are bend contours left in the sample, which is further evidence for residual strain, and thus plastic deformation of the samples. In addition, during unloading, after the force dropped to zero, the contours were still moving backward, which is an indicator of plastic deformation recovery. Very small sample size can decrease the brittle-to-ductile transition temperature to room temperature for some brittle materials [3][4], and room-temperature plasticity has been observed previously in different polytypes of SiC with different geometries due to phase transition [5], gliding of existing dislocations [6], amorphization [7], and other mechanisms.

In situ TEM nanoindentation tests of 3C-SiC irradiated at 600°C with 3.15 MeV carbon ions up to up to 5 displacements per atom (dpa) in the first one micron show different fracture behavior. In situ indentation along the irradiation profile probes different levels of radiation damage. Indenting at deeper irradiation depth with more irradiation damage (high dpa and larger diameter defects) causes quick and sharp crack and a small residual indent, while indenting at non-irradiation effected area causes a larger residual indent and more debris. These preliminary results suggest that irradiation induced defects make the sample more brittle and reduce its fracture toughness.

Reference:

11:30 AM CP01.09.05
In Situ TEM Studies of Mechanical and Electromechanical Properties of Individual InAs Nanowires

Lunju Zang1, Christoph Gammer2, Burak Ozdo1, Thomas Nordqvist3, Peter Krostrup4, Andrew Minor1,5, Wolfgang Jäger6 e and Eva Olsson7; 1Chalmers University of Technology, Gothenburg, Sweden; 2Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; 3Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4University of Copenhagen, Copenhagen, Denmark; 5Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 6Institute of Materials Science, Christian-Albrechts-University Kiel, Kiel, Germany.

Strain engineering of the electrical and optical properties of semiconductor nanomaterials is an effective way to tailor the performance of nanowire-based devices such as high-
InAs nanowires, both bare InAs nanowires and InAs/Ga$_2$O$_3$As core-shell nanowires, were used in the investigation. Simultaneous stress and current-voltage (I-V) measurements were enabled by an electrical push-to-pull (EPTP) device in a Hysitron P95 nanindentation TEM holder. In situ nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). Direct and quantitative stress, strain and electrical transport measurements were carried out on individual nanowires. The results showed that the resistivity of the InAs nanowires decreased continuously with uniaxial tensile stress. Large piezoresistance effect was found in InAs nanowires. However, bare InAs nanowires and InAs/Ga$_2$O$_3$As core-shell nanowires show different electromechanical behavior. The large piezoresistance effect is partly due to the small Young’s modulus of the nanowires (~11 GPa), but band gap narrowing of InAs is considered to be the main reason for the resistivity change. Moreover, despite apparent elastic deformation of the nanowires, significant inhomogeneous strain distribution within the InAs/Ga$_2$O$_3$As core-shell nanowires was unveiled by STEM-NBED strain mapping at different tensile stress levels. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures [1].

Financial support from Swedish Research Council and Nano Area of Advance and Energy Area of Advance at Chalmers University of Technology are acknowledged.


11:45 AM CP01.09.06
In Situ TEM MEMS-Based Tensile Nanomechanical Testing of Ultrathin Films Saurabh Gupta, Brad Boyce, Olivier Pierron and Sandra Stanoev; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2Sandia National Laboratories, Albuquerque, New Mexico, United States.

A MEMS based technique for in-situ TEM nanomechanical tensile testing of ultrathin films has been developed which allows for high magnification TEM observations of the deformation mechanisms in the thin film at the nanoscale while simultaneously measuring the macroscale behavior of the thin film quantitatively. Consecutive stress relaxation transients were performed in-situ in the TEM on ultrathin grained 100-nm-thick gold and 200-nm-thick aluminum films using this MEMS device. The plastic deformation in the gold films was observed to be mediated via intragranular dislocations originating from grain boundaries and was very localised. Local grain growth was also observed in the aluminium films in regions of severe plastic deformation along with dislocation pile-ups in some grains. The physical activation volume of the gold films was obtained around 3-15b$^3$ while activation volumes between 5-40b$^3$ were measured for aluminum films. The observed plastic deformation mechanisms are consistent with the low activation volumes calculated for these ultrafine grained thin films.

SESSION CP01.10: Materials in Extreme Design
Session Chair: Sasi Kumar Tippahotha
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 101 A

1:45 PM *CP01.10.01
High-Velocity Impact Ignition of Pre-Stressed Micron-Scale Aluminum Powder Compacts Michelle Panova and Kevin Hill; Texas Tech University, Lubbock, Texas, United States.

Pre-stressing aluminum (Al) particles is linked to increased reactivity by altering the physical and mechanical properties at the core-shell interface of the Al-Al$_2$O$_3$ particle. Changes in quenching rates during pre-stressing have been shown to change the reaction mechanism of micron Al particles. Faster quenching rates (i.e., 900 K/min) lead to shell delamination and a reduced oxidation barrier. Slower quenching rates (i.e., 200 K/min) result in increased hoop stress in the shell. To examine the effects of pre-stressing under high velocity (850-1200 m/s) impact conditions, 3-4.5 micron diameter Al particles were annealed to 573 K, then quenched at different rates (200 and 900 K/min), mixed with 1 wt. % polyvinylidene fluoride (PVDF), and formed into pellets. The projectiles were fired from a High-velocity Impact-ignition Testing System (HITS) into a steel anvil. Data for flame spreading and pressure in the impact chamber were collected for two stages of ignition and reaction corresponding with impact and rarefaction due to after blast. Results show that shell delamination in the faster quenched Al samples contributes to faster reaction rates during impact as well as during rarefaction in the after blast for both impact velocities. In contrast, increased hoop stress in the shell from slower quenching significantly delays energy release at the lower impact velocity by delaying shell failure. At the higher impact velocity, the increased stress in the slower quenched particles contributes to more rapid energy release than untreated particles during impact and after blast, but the alumina diffusion barrier is not removed as effectively from the particles compared to the delamination present in the faster quenched particles. These results establish a link between altering mechanical properties of fuel particles towards influencing fuel particle reactivity under the extreme loads of high velocity impact ignition and reaction.

2:15 PM CP01.10.02
Mechanical Characterization of Quartz Tuning Fork Coupled Oscillator for Quantitative Measurement of Nanoscale Forces at sub-10 nm Gap Separations Cedric Shaskey, Amun Jarzembski and Keunhan Park; University of Utah, Salt Lake City, Utah, United States.

Quantitative nanoscale force measurement using atomic force microscopy (AFM) has been well established [1]. However, these measurements are limited to cantilever-based AFM which suffers from a snap-to-contact when tip-sample separations are on the order of 10 nm. In order to probe forces when the tip-sample separation is in the sub-10 nm range, a force sensor which has vertical rigidity orders of magnitude larger than conventional AFM cantilevers is required. Quartz tuning forks (QTFs) satisfy this condition while also achieving higher sensitivity due to the coupled oscillation of their tines which produces a resonant Q-factor that is typically an order of magnitude larger than conventional AFM cantilevers. However, the coupled oscillation complicates the mechanical modeling and characterization. QTFs exhibit multimodal resonances: although previous models have accurately described the fundamental resonance [2, 3, 4], no model has been able to explain other observed resonant modes. The present study aims to create a lumped model capable of explaining all of the mechanical resonances of a QTF and extracting the relevant parameters. The QTF spectrum is measured electrically (via piezoelectric effect) and simultaneously measured optically (via Fabry-Perot interferometry). Electrical measurements are performed with two different lead configurations to separately extract the in-phase and anti-phase oscillations of the tines. Optical measurements are performed in two orthogonal directions to extract the true amplitude of the in-plane and out-of-plane oscillations. By combining these measurements with an in-plane model and an out-of-plane model, the lumped parameters can be extracted. Preliminary measurements indicate that the coupling is an order of magnitude larger than previously reported [3]. Complete characterization of the QTF will enable predictions of the behavior of the QTFs when a tip-sample interaction is present. This will allow quantitative extraction of the interaction force at sub-10 nm gap separations.

References:

2:30 PM CP01.10.03
Crack Nucleation in a 3C-SiC Nanowire and Its Atomistic Origin Fazle Flahi and Zubaer M. Hossain; Mechanical Engineering, University of Delaware, Newark, Delaware,
It is very important to predict the crack nucleation site to eliminate the probability of failure of a material. A thorough analysis of stress distribution on 3C-SiC (111) nanowire is done by Molecular Dynamics calculation to find out the atomistic origin of a crack nucleation. Stillinger-Weber interatomic potential is used to predict the stress on different locations of the hexagonal cross-section. In thin nanowires with a diameter (d) less than 1.0 mm has their highest stress concentration on core site. For the smallest nanowire considered in this work (d=0.32 nm), the difference in stress between the edge atoms and the core atoms is around 50 GPa. But as the diameter increases, the stress concentration moves to the immediate vicinity of the edge. For, d>1.0mm, core region is not subjected to highest load and crack nucleates in the immediate bond to the corner atom. The surface is a result of terminated material from the bulk structure and it is least stressed in larger nanowire when the external load is uniaxial along the (111) direction. Heterogeneity in stress on the cross section of NW is the sole contributing factor to the variation in crack nucleation site. As the nucleation of crack is directly related to toughness, we also get d-dependent toughness in nanowire due to stress heterogeneity. The concluding statement of this work is, the location of crack nucleation in 3C-SiC (111) nanowire and corresponding energy absorption rate is governed by stress heterogeneity, not the surface to volume ratio of the structure.

3:45 PM BREAK

SESSION CP01.11: Advances in Xrreme Experimentation—Synchrotron Micro XRD II

Thursday Afternoon, April 25, 2019

PCC West, 100 Level, Room 101 A

3:15 PM CP01.11.01
Coherent Diffraction for a Look Inside Nanostructures—Catalysis and Defects
Marie-Ingrid Richard1, 2, 3; IM2NP, Marseille, France; 1Aix-Marseille University, Marseille, France; 2ESRF, Grenoble, France.

Characterising the structural properties (strain gradients, chemical composition, crystal orientation and defects) inside nanostructures is a grand challenge in materials science. Bragg coherent diffraction imaging (Bragg CDI) can be utilised to address this challenge for crystalline nanostructures. A resolution of the structural properties of less than 10 nm is achieved up to-date [1]. The capabilities of the Bragg CDI technique will be demonstrated on single nanoparticles for enhanced catalysis.

As an example, the Bragg CDI technique allows understanding the interplay between shape, size, strain, facetting [2], composition and defects at the nanoscale. We will demonstrate that Bragg CDI on a single particle model catalyst makes it possible to map its local strain/defect field and directly images strain build-up close to the facets. The localized strain modfies sorption energies of the reactants. In situ [3] and operando Bragg CDI was also performed: it was possible to track a single particle in liquid and gas phase environments, to monitor its facet changes and to measure its strain response to gas or electrochemical reaction.

This technique opens pathways to determine and control the internal structure of nanoparticles to tune and optimise them during catalytic and other chemical reactions.


Financial support to this work by ANR Charline (ANR-16-CE07-0028-01) is gratefully acknowledged.

3:45 PM CP01.11.02
Mechanical Strengthening of Nickel Continues Down to 3 nm
Bin Chen1, Xiaoling Zhou1,2, Qiong Xu1, Z.Q. Feng1, L.L. Zhu1, X.X. Huang1, and X.X. Huang1, 2, 3

Because of unique sensitivity to lattice, Bragg coherent x-ray diffraction imaging (BCDI) has been employed on various nanoscaled materials such as metal, metal oxide, and mineral, to image three dimensional map of strain distribution and lattice distortion with non-destructive measurements. In-situ and operando imaging became a major driver for BCDI to address scientific questions on physics, chemistry, and materials science in recent years.

In this talk, I will introduce current state-of-art of BCDI and recent experimental results on in-situ and operando BCDI. High temperature BCDI reveals annealing effect on gold grain on thin film and relaxation of strain inside quantum materials such as nanodiamond and silicon carbide. Strain and dislocation development has been observed on palladium during phase transition under hydrogen flow and on gold-silver alloy for dealloying process. In addition, some estimates of BCDI in the future will be discussed.

4:15 PM CP01.11.03
In Situ and Operando Studies Using Bragg Coherent X-Ray Diffraction Imaging
Wonsuk Cha; Argonne National Laboratory, Lemont, Illinois, United States.

Because of unique sensitivity to lattice, Bragg coherent x-ray diffraction imaging (BCDI) has been employed on various nanoscaled materials such as metal, metal oxide, and mineral, to image three dimensional map of strain distribution and lattice distortion with non-destructive measurements. In-situ and operando imaging became a major driver for BCDI to address scientific questions on physics, chemistry, and materials science in recent years.

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4:30 PM CP01.11.04
Novel Functional Nanocomposites of 2D MXenes and Light-Weight Metals
Vladislav Karnyshayev1, Babak Anasori2, Yury Gogotsi2 and Dmitri Talapin1; 1The University of Chicago, Chicago, Illinois, United States; 2Drexel University, Philadelphia, Pennsylvania, United States.

Nanocomposites of light-weight metals and ceramic Nanocrystals (NCs) as reinforcements are an important class of structural materials. Compared to other ways of fabricating these materials, liquid metal route results in nanocomposites with superior mechanical properties, greater industrial compatibility and chemical versatility. From thermodynamic
point of view, introducing ceramic NCs directly into liquid metal is challenging because surface tension of liquid metals greatly exceeds that of ordinary solvents. Hence, in order to satisfy the wetting condition, strong chemical bonding between NCs and liquid metal is required. At the same time, the interfacial reaction should not compromise thermodynamic stability of the NCs. Among existing ceramic NCs, the recently discovered 2D transition metal carbides (MXenes) offer a unique solution to fabricating next generation light-weight nanocomposites due to their high-strength (Young Modulus 0.33 TPa), metal-like conductivity, solution-processability and surface group tunability. Here we demonstrate that 2D sheets of titanium carbide (Ti$_3$C$_2$Tx, where T stands for surface groups such as =O, -OH and -F) can be successfully integrated into ultra-light-weight Mg-Li alloy (final density $\rho \approx 1.8$ g/cm$^3$) via the liquid metal route. 2D sheets are uniformly distributed throughout the Mg-Li alloy matrix as evidenced with FIB-SEM and TEM analysis. The recovered NCs retain 2D morphology and ultrathin thickness of the starting MXene sheets ($\approx 1$ nm) and can be preliminarily indexed as a face-centered cubic Li alloy (final density $\rho \approx 1.8$ g/cm$^3$).

PARC has recently invented a novel composite, Chemically Linked Graphene Networks, wherein graphene sheets are chemically bonded to each other by flexible polymer linkers. Inter-particle chemical bonding restricts their movement under stress. This feature cannot be achieved with conventional particle-filled polymer composites in which the dispersed particles can move easily within the polymer network on impact or load. Chemically linked graphene networks produced cured architectured structures with remarkably high strength when compared with the base polymers or with conventional graphene composites. These structures are enabled by a new, low cost synthetic approach to highly dispersible, chemically reactive functionalized graphene particles. In addition to enhanced mechanical strength, we have found that this material possesses additional valuable properties including outstanding gas barrier performance and high thermal conductivity. The technology is targeted for direct 3D printing of multifunctional lightweight load-bearing structural parts that may be used as a direct carbon-fiber reinforced polymer replacement, or as a replacement for some metal parts in industries such as aerospace and automotive.

**REFERENCES**

Studies of MOFs and Their Complexes by High Resolution "Conventional" and Novel Solid-State Synchronous Fluorescence Spectroscopy

Nc metals have been reported to exhibit an extended microplastic regime during loading unlike in case of the cg metals that show a macroscopic yielding already at 0.2% strain [3]. In addition, these materials have been shown to exhibit Bauschinger effect (BE) during unloading, where a pronounced reverse plastic deformation is observed [4]. So far, such an effect has been explained by stress gradients developing between differently sized grains or by back stresses that develop due to piling up of dislocations at grain boundaries that aids their reverse motion during relaxation [5,6]. However, in case of nc metals it is still a subject of open discussion whether the deformation processes are mainly dislocation or grain boundary mediated. Thus, in the context of cyclic loading-unloading, we intend to explore the deformation mechanisms that contribute to the BE in these class of materials.

We performed in situ cyclic loading-unloading experiments on 100 nm thick sputtered nc Pd thin films inside a TEM. The stress strain curves show a nonlinear unloading deviating from ideal elastic unloading behavior, which is a characteristic of the BE reported in case of thin metal films. The corresponding bright field TEM (BFTEM) series show local contrast changes in the grains, which are partly reversible during unloading. Aiming towards a quantitative un-parsing of these events, we used automated crystal orientation mapping in STEM mode (ACOM-STEM) in conjunction with quasi static loading-unloading experiments. Analyses of series of HAADF-STEM images that were acquired along with the ACOM series indicated reversible contrast changes in several grains indicating changes in crystal orientations. This was confirmed from the quantitative analyses of the ACOM series consisting of a large number of grains that indicated grain rotation. The average rotation was found to progressively increase during loading while a significant number of grains showed complete or partially reversible rotations on unloading. Local analyses of the STEM series also shows that the contrast changes traverse multiple grains in direct vicinity indicating that these rotations are likely to be operating in a co-operative manner. Relating these effects to the observed mechanical response of the sample, we conclude that grain rotation is a potential mechanism contributing to the BE in nc metals. With our in situ ACOM approach, we are developing a closer link of the competing deformation mechanisms and the microstructural heterogeneity in terms of grain size, crystallographic texture and grain boundary character to further elucidate on the observed mechanical response of nc metals.


8:45 AM CP01.12.03

Imaging Reversible Topotactic Phase Transitions in Strontium Ferrite Thin Films by In Situ TEM Zhenzhong Yang, Le Wang, Endong Jia, Zihua Zhu, Chongmin N. Wang, Peter V. Sushko and Yingge Du; Pacific Northwest National Laboratory, Richland, Washington, United States.

The creation, clustering, and ordering of oxygen vacancies (VOs) in perovskite-structured oxides (ABO3, B being a transition metal) give rise to a special class of materials, such as Brownmillerite (BM) structured SrCoO2-x SrFeO2-x and rhombohedral structured SrCrO2. A topotactic phase transition (e.g., SrFeO2-x ↔ SrFeO3) can occur as a result of oxygen content variation, which leads to dramatic changes in their functional properties, such as electronic conductivity, ionic conductivity, and electrocatalytic reactivity. Understanding the detailed structural and phase transition processes is critical for the rational design of functional energy materials that are used in batteries and solid oxide fuel cells. In this study, using in situ environmental transmission electron microscopy (ETEM), we directly imaged the oxygen diffusion and phase transition processes in epitaxial BM-SrFeO2-x thin films at elevated temperatures. The high spatial and temporal resolution of the TEM allowed us to correlate the onset of phase transition, reaction rate, and transition pathways with the annealing temperature. The phase transformation from BM-SrFeO2-x to perovskite SrFeO3.6, triggered by the intercalation of O ions, exhibited a clear reaction front, indicating the oxidation of FeO tetrahedra to FeO octahedra occurs preferentially at the phase boundaries, which is supported by our density functional theory calculations.

9:00 AM CP01.12.04

Studies of MOFs and Their Complexes by High Resolution “Conventional” and Novel Solid-State Synchronous Fluorescence Spectroscopy Cole Grinnell1, Jun Dai2, Michael L. McKee1 and Alexander Samokhvalov1; 1Chemistry Department, Morgan State University, Baltimore, Maryland, United States; 2Chemistry Department, Rutgers University, Camden, New Jersey, United States; 3Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama, United States.

High resolution optical spectroscopy and, specifically, fluorescence spectroscopy provides valuable information on both vibrational and electronic phenomena. This is of significant interest to understand from vibrionically resolved optical emission spectra the mechanisms of intermolecular interactions of functional groups in advanced nanoporous solid-state materials, in particular metal-organic frameworks (MOFs), and their complexes with small molecules. First, we will describe our recent studies of vibrionically resolved solid-state “conventional” fluorescence emission spectra of naphthalene at room temperature. Distinct vibrionic transitions 0-0, 0-1, 0-2, etc. are facely observed in the near-UV range, and assigned to specific vibrations of isolated naphthalene molecules. In addition, naphthalene forms excimers, which is clearly seen in well-resolved vibronic structure in the near-UV/visible range of fluorescence spectrum. Further, naphthalene forms the stoichiometric sorption complex with MOF Basolite F300. In this research, we utilized naphthalene molecule as the fluorescent “self-probe” confined in the nanocavity of MOF, which shows: a) a loss of excimer emission, b) the decrease of area ratio A(0-2)/A(0-1) of respective vibronic peaks, and c) non-polar environment. The complementary characterization of chemical bonding in the complex has been conducted using UV-Vis DRS and DFT calculations. However, “conventional” fluorescence emission spectra of most solids are very broad and diffuse under ambient conditions, therefore their vibronic structure is not observed. For chemical compounds in diluted solutions, strong narrowing of emission peaks is routinely achieved by synchronous fluorescence spectroscopy (SFS). In the experiment by SFS, the excitation λexc and emission λem wavelengths are scanned simultaneously (“synchronously”) at the constant offset Δλ = λexc - λem. In contrast, studies of solid materials by the SFS are very rare. We present novel high resolution in-situ instrumental method, solid-state synchronous fluorescence spectroscopy, which has recently been developed in our lab. This method has been applied for studies of electronic photoexcitation/relaxation transitions and molecular interactions within MOFs and their sorption complexes. The MOF Basolite A100, which is similar to the benchmark MIL-53(Al), shows the unprecedented and sharp, “molecular-style” resonances in solid-state synchronous fluorescence spectra. Basolite A100 forms the stoichiometric sorption complex with an archetypal polar molecule of dimethyl sulfoxide (DMSO). The peaks in the solid-state SFS of the sorption complex are shifted to the shorter wavelengths, due to the interactions of the linker in this MOF with DMSO adsorbate molecule. The complementary experiments by powder XRD, FTIR and differential scanning calorimetry (DSC) provide an additional insight on the nature of bonding in the complex. The described novel high resolution spectroscopic method, solid-state SFS shows strong potential to become a useful experimental technique for studies of electronic levels in solids, the pathways of excitation and relaxation, and for understanding intermolecular interactions in composite functional nanostructured materials well beyond MOFs and their sorption complexes.

9:15 AM CP01.12.05

Synthesis and Mechanical Behavior of Freestanding, Nanocrystalline NiTi Films Under Cyclic Tensile Deformation Paul Rasmussen and Jagannathan Rajagopalan; Arizona State University, Tempe, Arizona, United States.

Controlling the micro/nanostructure of thin films would enable us to explicitly tailor their mechanical behavior. Here, we describe a new process to synthesize thin films with precise microstructural control via systematic, in-situ seeding of nanocrystals, and subsequent crystallization of amorphous precursor films. Using this process, we synthesized austenitic NiTi films with submicron grain sizes. We then co-fabricated freestanding samples of the films with MEMS testing stages and performed cyclic tensile load-unload experiments. Samples seeded with Cr showed a high phase transformation stress (> 700 MPa) during the first cycle that increased even further during subsequent cycles. More interestingly, the film showed a continuous decrease in stress-strain slope during unloading rather than the pseudo-elastic behavior typically observed in nanocrystalline NiTi. Preliminary in-situ TEM straining studies suggest that this unusual loading behavior is caused by a combination of reverse phase transformation and reverse plasticity.

9:30 AM BREAK
In Situ Studies of Surface Effects on the Mechanics of Metal Network Structures

Joerg Bagdahn; Anhalt University of Applied Sciences, Köthen (Anhalt), Germany.

The topic of soiling of photovoltaic module (PV) and concentrated solar power (CSP) collectors has recently gained increasing attention due to its impact on solar power production, especially in arid and semi-arid areas with high concentrations of airborne dust. Soiling describes the deposition of dust and other contaminants on surfaces, reducing solar irradiation by absorbing or reflecting the sunlight, causing energy yield losses which can exceed 1% per day. The amount of soiling is influenced by complex interactions of many factors which can vary significantly from site to site. Dust accumulation and corresponding soiling rate is determined by the interaction of particle deposition, rebound and resuspension, which are strongly influenced by particle adhesion forces and removal forces.

A focus is made on soiling mechanisms that increase particle adhesion such as cementation, particle caking and capillary aging. A detailed analysis and model of dew-driven soiling mechanisms of cementation, particle caking, and capillary aging are given on the basis of microstructural material and dust characterization of outdoor exposed glass samples. To identify the underlying physical and chemical processes of cementation, glass samples were exposed to outdoor conditions in various locations (Qatar, Chile, Morocco) and investigated at microstructural level using electron microscopy (SEM and TEM) and elemental analysis with energy-dispersive X-ray spectroscopy (EDX). For samples from Qatar, the formation of nanoscopic needle-like structures was observed, which can be attributed to the clay minerals and somehow contradicts the common perception that cementation occurs via the precipitation of salt.

Overall the study aims to provide a useful, in-depth but also global overview and fundamental understanding of soiling processes on PV modules down to the microscale, which could be used to develop appropriate soiling mitigation strategies.

Stress and Fracture of Crystalline Silicon Cells in Solar Photovoltaic Modules—A Synchrotron X-Ray Microdiffraction Based Investigation

Sasi Kumar Tippahothla1, Wenjian J. Song1, Ihor Radchenko1, Camelia V. Star1, Nobumichi Tamura2, Andrew A. Tay2 and Arief S. Budiman1; 1Singapore University of Technology and Design, Singapore; 2Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Fracture of crystalline silicon solar cells in photovoltaic modules is a big concern to the photovoltaics (PV) industry. Cell cracks cause performance degradation and warranty issues to the manufacturers and hence, they are a limiting factor to the applicability of silicon PV as a main stream power source with high long-term reliability. In such a scenario, it is important to evaluate and quantify the fracture of the crystalline silicon cells to address it. The roots of the cell cracking process lie in the manufacturing and integration process of the cells and modules as they go through a series of elevated temperature and pressure processes, involving bonding of dissimilar materials, causing thermomechanical stresses, thus leading to cell fractures. Evaluation of the mechanics of these thermomechanical stresses and the role of different materials and processes in a sequential manner is highly essential to quantify these stresses and optimize the PV modules to address them and hence, the cell fractures. We present a novel synchrotron X-ray microdiffraction based techniques combined with finite element modelling to evaluate and characterize the stress and fracture in the crystalline silicon PV modules. Our results show that the thermomechanical stress builds up over the module integration processes such as soldering and encapsulation. We show the detailed stress evolution at each step of the lamination process, using the finite element simulations, validated by the synchrotron X-ray microdiffraction results. We further show the effects of the material and process parameters which affect the cell stress and thus, could be used to reduce the cell fractures and pave the way for the next generation crystalline silicon solar PV modules with enhanced fracture resistance.

Advances in X-Ray Microscopy for the Study of Battery Reactions in Single Particles

Joeri Cabana; University of Illinois at Chicago, Chicago, Illinois, United States.

The existing performance limitations of Li-ion batteries can be tracked to slow transport and irreversibilities in the changes undergone by the electrode materials, often coupled with mechanical events such as fracture. Tools that provide insight into the onset and propagation of these transitions are critical to identify the mechanisms of electrochemical function. This information must be generated at the level of single particles, where irreversibilities trigger degradation of the electrode architecture. Synchrotron-based X-ray microscopy combines morphological observations at high spatial resolution with a suite of chemical probes, such as diffraction and spectroscopy. Therefore, it is ideally suited to relate electrochemical observations with changes in nanoscale chemistry, linked to mechanical degradation. In this talk, we will justify the need for sophisticated connections between these phenomena, and we will proceed to discuss recent developments in X-ray microscopy aimed at visualizing them in single particles of battery electrodes. The talk will highlight the new fundamental insight generated by the tools, involving local dynamics of heterogeneity and, where relevant, their relationship with fracture events. While significantly valuable insight will be gleaned from samples harvested at relevant points of the electrochemical reaction, these measurements create uncertainty due to the possibility of relaxation of components from the kinetically controlled functional state to one that is more stable under open circuit conditions. Therefore, we will introduce our latest efforts to carry out time-resolved measurements simultaneous to the electrochemical reaction.

Creep Behavior of Nanocrystalline Al Alloys

Sung Eun Kim, Nisha Verma, Pascal Bellon and Robert S. Averback; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Nanostructured alloys are currently of much interest for their potential applications in extreme environments. Most research has focused on their high strength and ductility, however, for high temperature applications, their susceptibility to creep damage is also important, and much less work has been performed on this topic. Creep may be significant in these materials as diffusional creep scales inversely with grain size, e.g., Coble creep varies as 1/r3, and in situ creep measurement is one of the techniques highly demanded these days.

In the current work we have examined grain growth and creep behavior in Al alloys- Al5Si, Al5Si5 and Al5Si7- using our in-situ creep measurement apparatus. We prepared our alloys as thin films using magnetron sputtering. These films were stabilized at a grain size ~150 nm by first annealing them at 250°C. Creep measurements were performed using a bulge test (JJ Vlassak and WD Nix, J. Mats. Res. 7, 3242, (1992)); the grain size and precipitate structure were examined by transmission electron microscopy. The creep measurements revealed that the creep rate increased linearly with applied stress, while the temperature dependence showed approximately Arrhenius behavior with an activation enthalpy of 0.2 – 0.5 eV, which is somewhat lower than that of grain boundary diffusion in large grained Al.
small scale has been linked to interfacial effects, as there are observations of stiffening or enhanced compliance in nanoscale objects. Yet, the underlying mechanisms remain under investigation. While numerical studies provide a wealth of suggestions, meaningful experimental verification is more elusive. This talk discusses experiments designed to verify the suggested contribution of capillary forces to the plastic and elastic response of small bodies. Dealluying-made nanoporous metals provide model systems in the form of homogeneous metal networks with struts or ligaments at the nanoscale. The mm-size nanoporous bodies are highly deformable in compression and can be tested with reliable macroscopic methods. In-situ tests of such samples in electrolyte and control of the electrode potential afford variations of the surface state during ongoing deformation processes. Typically, the variation of surface state tension and surface stress are known; the response of the mechanical behavior then affords robust conclusions on the role of capillary forces in small-scale mechanics, including their impact on strength, compression-tension asymmetry, and size-dependent stiffness. At the same time, electrochemical cycles can be tuned to provide a stringent control over the purity of the surface, which is rarely available in experiments in the field.

2:15 PM *CP01.14.02
Deformation and Failure of CuZr Gradient Nanoglasses Paulo Brancicio; University of Southern California, Los Angeles, California, United States.
The intricate deformation and failure of seamless gradient nanoglasses are investigated with tensile loading large-scale molecular dynamics simulations. Cu55Zr45 metallic glasses are used as parent alloys for the construction of functionally graded nanoglasses with grain sizes from 3 to 15 nm. Tensile loading simulations are used to characterize the mechanical behavior of the heterogeneous metallic glass and shed light on the plastic deformation mechanisms. Results indicate a strong localization of the plastic deformation beyond the yield point for loading parallel to the gradient direction in soft regions with high concentration of reduced grain sizes. Loading perpendicular to the gradient direction indicates overall significant delocalization of plasticity throughout the sample. Results indicate a synergy of the gradient design and a superior combination of strength and ductility for gradient nanoglasses with a hard core (large grain size) compare with gradient nanoglasses with soft core (small grain sizes), in agreement with reports for gradient nanocrystalline systems.

2:45 PM CP01.14.03
Electrical and Mechanical Tuning of 3D Printed Photopolymer-CNT Nanocomposites Through In Situ Dispersion Jaime E. Regis1, 2, Luis Chavez1, 2, Luis C. Delfin1, 2, Carlos Garcia Rosales1 and Yirong Lin1, 2, 1Department of Mechanical Engineering, University of Texas at El Paso, El Paso, Texas, United States; 2W.M. Keck Center for 3D Innovation, The University of Texas at El Paso, El Paso, Texas, United States; 3Department of Electrical and Computer Engineering, The University of Texas at El Paso, El Paso, Texas, United States.
In recent years, polymer matrix nanocomposites have gained an increased amount of interest due to the scalability and manufacturability provided using polymers and the highly desirable properties from their fillers. The incorporation of ceramic, metallic, and/or organic fillers have given way to a variety of applications by enabling the improvement of thermal, electrical, mechanical, and dielectric properties. Such applications include, but are not limited to, energy storage materials, piezoelectric pressure sensors, and self-healing materials. Due to their high electrical conductivity and mechanical properties, carbon nanotubes (CNT) have attracted a great amount of attention for use as nanocomposite reinforcement; however, the fabrication of composites of this nature through additive manufacturing is a concept that has not been explored thoroughly. CNT have the tendency to agglomerate and become points of failure for composites rather than the reinforcements. For this reason, additive manufacturing of CNT-polymer nanocomposites typically uses low percentages of CNT. In this study, the synthesis and fabrication of multi-walled carbon nanotubes (MWCNT) composites was realized through stereolithography additive manufacturing with in situ, electric field-assisted dispersion. With the introduction of MWCNTs into the polymer, a 77% increase in elastic modulus was observed. Furthermore, in situ dispersion through electric field improved the average elongation at break of the samples with MWCNTs by 32%. An increase in ultimate tensile strength of the MWCNT from in situ dispersed composites of 42%, more than 20% over the pure polymer material, was also observed when applying an electric field. Engineering of the magnitude and direction of electrical conductivity in MWCNTs was accomplished through the application of in situ electric fields during the 3D printing process. The electrical conductivity of the material saw an increase of 50% with the introduction of MWCNTs which improved further by 26% with electric field induced dispersion. The feasibility using in situ electrical field in 3D printing to tune electrical and mechanical properties of MWCNT reinforced, polymer nanocomposites was demonstrated.

3:00 PM BREAK

SESSION CP01.15: Advances in Novel and Extreme Materials Design—Polymer/Fibre-Based Nanocomposites
Session Chairs: Paulo Brancicio and Arief Budiman
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 121 A

3:30 PM CP01.15.01
3D Architectural Design Enabled by Electrospinning to Fabricate Strong and Tough Fibers Komal Agarwal1, Rahul Sahay2, Aviniah Bajir3 and Arief S. Budiman1, 2 Singapore University of Technology and Design (SUTD), Singapore, Singapore; 3Department of Engineering, School of Engineering and Mathematical Sciences, La Trobe University, Melbourne, Victoria, Australia.
Advances in material science and engineering has bolstered technological advancements of the twenty first century. Nature constantly provides solutions to overcome materials and structures related obstacles. Cuticle of Mantis shrimp dactyl club, scarabaeus, lobster, and epicarp of diplazium crenatoserratum and pollia condensata fruit, have inspired scientists to mimic their microstructure for enhanced optical and mechanical properties. The structural arrangement of the fiber layers plays crucial role in enhancement of toughness of the composite. In past, attempts have been made to design helicoidal structures at macroscopic levels. We have successfully fabricated helicoidally oriented fibers in microns range (20-25 microns) using near field electrosprinning. For our first study, melt near field stage-controlled electrosprinning was used to assemble dense Polyacryloplactone (PCL) fibers (150-200um) stacked helicoidally at 15° angle offsets. The toughness of the surface-treated helicoidal PCL was found to be two times higher than the surface-treated unidirectional sample and five times higher than the helicoidal sample without surface treatment. Alternatively, in our second study, near field solution electrosprinning was used to fabricate much smaller (av. ~22μm) Polyvinylidene fluoride (PVDF) fibers fused together and oriented at angle offsets of 15°. Numerous interface changes between different planes and directions, arrests crack propagation in helicoidal layers, allowing material to absorb more energy before fracture. These fibers show superior tensile characteristics, impact resistance and toughness as compared to its bulk counterparts. Near field electrosprinning provides a promising future pathway to fashion helicoidal architectures in nano range increasing the toughness and impact resistance of the materials furthermore.

3:45 PM CP01.15.02
Multi-Phase Graphene-Polymer Nanocomposite Fibers—Design, Fabrication and Characterizations Weiheng Xu, Sayli Jambhulkar and Kenan Song; Arizona State University, Mesa, Arizona, United States.
Polymer fibers usually possess high tensile strength, anti-corrosion, and heat resistance properties. Combining them with “nanofillers”, such as graphene, would further introduce and enhance properties including mechanical reinforcement, energy dampening, electrical conductivity and thermal dissipation. Most of the previous works in this area involved homogeneously mixing graphene or graphene oxide (GO) dispersions in polymers, following by chemical or thermal reduction. However, the finalized graphene nanoparticles are not, strictly speaking, single-layered due to their tendency to aggregate during the mixing process and forming defects and unoxidized functional groups during post reduction. Besides, graphene particles are not always continuously bridged and their orientations are not anisotropic, leading to the limited mechanical strength, thermal and electrical conductivity in composite fibers. We are currently working on a cost-efficient method suitable for mass production of single-layered graphene-included polymer composite (GPC) fibers through an in-situ graphite exfoliation method. During the fabrication process, spinnertet was designed and fabricated to include polymers and original graphite in different channels. The relative molecular movements on two sides of the graphene channel can initiate and promote graphene exfoliation and orientation in a higher degree than those composite fibers with only polymers appearing on one side of the graphite. Upon stretching the spun fibers, polymer channels separated by the graphene channel will generate shear stresses, the degree of which will depend on polymer-graphene interfacial bonding and relative displacements of molecular chains on both sides of graphene layers, along with the graphene channel direction. Mechanical tests showed an increase of both modulus and strength (>200%) as comparing multi-phase composite fibers with pure polymer fibers. Scanning electron microscopy
3D Printable High-Performance Cyanate Ester Resins for Additive Manufacturing and hematite nanomaterials and in understanding processes controlling iron mineral transformations in the environment. The findings provide detailed new insights into processes controlling phase transformation outcomes among iron (oxyhydr)oxides, and should help in the design new maghemite larger particles during heating, allowing us to discover and observe the size effect among individual nanowires. Both transformed into hematite. For the sized β-FeOOH nanowires. In this case diameters larger than 20 nm, the final product depends on the heating temperature, time, and pressure. Maghemite was the final product at transformation temperatures less than 300 °C, whereas hematite was the final product above 300 °C. The transformation of maghemite to hematite appeared to be by direct topotactic atomic rearrangement in the solid state. Imaging was complemented by in situ XRD, in situ XPS and TGA-mass spectrometry measurements. In situ XRD showed amorphization of the β-FeOOH nanowires quickly upon approaching 200 °C and then maghemite was observed, consistent with the in situ TEM observation. However, the recalcitrance of maghemite conversion to hematite when starting from smaller β-FeOOH nanowires did not manifest in the XRD measurements upon increasing the heating temperature to 500 °C, which occurred readily for all different sized β-FeOOH nanowires. In this case ex situ TEM indicated the smaller β-FeOOH nanowires merged into larger particles, which allowed the maghemite to be readily transformed into hematite. For the in situ TEM experiments, because the β-FeOOH nanowires were mounted on a copper grid, this appeared to inhibit nanowire coalescence into larger particles during heating, allowing us to discover and observe the size effect among individual nanowires. Both in situ XPS and TGA-MS measurements showed the loss of water and HCl upon heating. The findings provide detailed new insights into processes controlling phase transformation outcomes among iron (oxyhydr)oxides, and should help in the design new maghemite and hematite nanomaterials and in understanding processes controlling iron mineral transformations in the environment.

4:30 PM CP01.15.05
3D Printable High-Performance Cyanate Ester Resins for Additive Manufacturing Seyed Mahmoud Hosseini and Walter E. Vott; Chemistry, The University of Texas at Dallas, Richardson, Texas, United States.

Cyanate ester resins (CER) are a class of high-performance thermosetting resins with low dielectric constants, high glass transition temperatures (~250°C), and very low water absorption. Cyanate ester polymer’s strength, rigidity, chemical resistance, and ability to withstand extremely high temperatures make them ideal for use in applications in which long-term stability is essential. For instance, cyanate ester polymers are used in the development of electronic devices, under-the-hood automobile parts, and in aerospace applications and vehicles. However, the bottleneck of pure CE resins is their brittleness due to limited strain tolerance. One of the ways to overcome this problem is copolymerizing cyanate esters with epoxy resins, which improve the flexibility and decrease the curing temperature. One current method to prepare 3D structures of cyanate ester-epoxies is a molding process that involves casting monomers into a mold and then heating up the mold gradually. This study shows the synthesis and development of resins for the 3D printing of cyanate ester with different thiol-based monomers. We could overcome obstacles that had been preventing the field from efficiently using three-dimensional printing to create cyanate ester polymers. We could improve the brittleness of cyanate ester polymers with tunable glass transition temperature. Additional additives (initiators, inhibitors, and dyes) and monomers containing photo-cross-linkable groups provide control of chemical crosslinking for spatial control during network gelation.
Growth of single crystals via assembly of colloidal nanocrystals is widespread phenomenon in both synthetic and natural environments. In mineral systems, this process exhibits a range of styles including face-specific oriented attachment of like phases, attachment of a nanoscopic phase to a bulk phase followed by transformation, and mis-oriented aggregation followed by coarsening to a single crystal. While descriptions of assembly in these systems must share a commonality with continuum-based DLVO-type theories for simple colloids, mineral systems present additional complexities, including face-specificity of dielectric properties, the presence of structured nanoscale interfaces, and the consequent solvent-responses that are expected to be of a comparable length scale. To understand the relationship between nanocrystal structure, interparticle forces and consequent motion leading to assembly, we are investigating colloidal assembly in the titanium, iron and zinc oxide systems. We use in situ TEM to observe assembly dynamics, force spectroscopy with custom-made single crystal tips to measure face-specific interparticle forces, AFM to probe interfacial structure, and molecular simulations to understand the origins of these features. For both ZnO and the iron oxhydroxide ferrhydrate, TEM demonstrates that direction-specific forces align randomly diffusing particles prior to contact and that attachment occurs on lattice matched faces via a sudden jump to contact followed by coarsening to produce compact single crystal structures. Direct measurements of the forces between both TiO$_2$ and ZnO surfaces reveal orientation dependent attractive interactions that exhibit the symmetry of the underlying lattice. A combination of molecular dynamics and classical DFT simulations indicate a combination of hydration, ion correlation and dispersion forces are responsible for orienting the particles and that the barriers caused by hydration layers, which scale with surface hydrophobicity, cannot be overcome by simple Brownian motion in the absence of fluctuations in those layers. Addition of organic ligands, like oxalate, to the ferrhydrate system produces a dramatically different pathway and outcome: Nanoparticles of hematite nucleate sporadically from the ferrhydrate and, once formed are covered with oxalate and drive all new hematite particles to nucleate within about 1 nm of the surface, after which they jump to contact. The oxalate inhibits growth and coarsening of the particles, leading to spindle-shaped aggregates of coaligned particles with a fixed and constant aspect ratio. Thus the random assembly process seen in the pure ferrhydrate system is replaced with one that is deterministic. Classical DFT calculations show that gradients in Fe$^{2+}$ chemical potential created by the ligands drive this interfacially driven bias towards growth by oriented attachment.

SESSION CP02.01: Crystal Nucleation and Growth, Nanoparticle Superlattice

10:30 AM • CP02.01.01
Understanding the Relationship Between Interfacial Structure, Interparticle Forces and Assembly Dynamics During Oriented Attachment of Colloidal Crystals

James L. De Yoreo$^1$, Lili Liu$^1$, Guomin Zhu$^1$, Xin Zhang$^2$, Dongsheng Li$^1$, Sebastian Kerstel$^1$, Maria Sushko$^1$, Jaehun Chun$^1$, Elias Nakouzi$^1$, Chongmin N. Wang$^1$, Greg Schenter$^1$, Kevin Rosso$^1$ and Christopher Mundy$^1$: 1Pacific Northwest National Laboratory, Richland, Washington, United States; 2Materials Science and Engineering, University of Washington, Seattle, Washington, United States; 3Chemical Engineering, University of Washington, Seattle, Washington, United States.

The directed assembly of nanoscale building blocks into complex superstructures is of widespread scientific and technological interest. Scientists and engineers have been intrigued by the prospects of tailoring self-assembled processes to create materials whose properties and function can be tuned through the interaction between constituent particles. In particular, recent reports of epitaxially connected colloidal quantum dot superlattices with long-range atomic coherence have generated significant interest as a platform for novel, quasi 2D ‘designer materials’. Experimental protocols for the formation of high quality superlattices in which constituent quantum dots are registered to within a single atomic bond length have been established; however, significant gaps persist in our fundamental understanding of several aspects of the underlying mechanism by which these structures form.

Our approach to gain mechanistic insights into the assembly and subsequent attachment leverages unique in-situ multiprobe characterization techniques including TEM and X-ray scattering. The combination of in-situ wide- and small-angle X-ray scattering informs the temporal evolution of nanoparticle orientation and assembly at the fluid interface. We will present recent advances with in-situ analysis TEM analysis of quantum dot solids deposited on a heating chip to gain atomic-level insights into the formation of the interdot bond. In-situ TEM experiments at varying temperatures and ramp rates hold significant potential to provide new mechanistic insights into the temporal evolution of interdot bridge width and structure.

11:45 AM • CP02.01.04
In Situ Cooling TEM Study on Structure Phase Transition in LaNiO$_{3-\delta}$

Xue Rui$^1$, Bixia Wang$^2$, Daniel Phelan$^1$, John Mitchell$^1$ and Robert Klue$^1$; 1Materials Science and Engineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Argonne National Laboratory, Lemont, Illinois, United States.

In the past decades, rare-earth nickelate perovskite RNiO$_3$ (R=rare earth) have been demonstrated to exhibit rich phase diagram concomitant with complicate magnetic property. It has been found that these nickelates can undergo a structure transition from Orthorhombic to Monoclinic (Pnma to P2$_1$/c) accompanied with metal-insulator transition (MIT) upon cooling process. Currently, atomic-resolution scanning transmission electron microscopy (STEM) equipped with a cooling holder can enable imaging with picometer resolution at cryogenic temperature, providing an intuitive method to analyze the change of atomic structure at low temperature. In this work, we will use aberration-corrected STEM combined with in-situ cooling to analyze the phase transition found in LaNiO$_{3-\delta}$. During in-situ cooling experiment, we have found the reversible disappearance/appearance of superlattice peak from diffraction pattern of LaNiO$_{3-\delta}$ as a function of temperature. Electron energy-loss spectroscopy (EELS) will be used to examine the change in local electronic structure as a function of temperature.
1:30 PM *CP02.02.01

**Self-Assembly of Electrostatically and Sterically Stabilized Colloidal Nanocrystals—The Roles of Topology, Image Charges and Non-Classical Nucleation**

Erik Janke, Igor Coropceanu, Michael Boles and Dmitri Talapin; Department of Chemistry, University of Chicago, Chicago, Illinois, United States.

Colloidal nanocrystals offer a route toward engineering new classes of materials by acting as discrete units that can be assembled to construct composite solids. The self-assembly of two sizes of spherical nanocrystals has revealed a surprisingly diverse library of structures. To date, at least fifteen distinct binary nanocrystal superlattice (BNSSL) structures have been documented. The stability of the observed binary phases cannot be fully explained using the traditional conceptual framework treating the assembly process as entropy-driven crystallization of rigid spherical particles. We evaluate new theoretical models treating the co-crystallization of deformable spheres and to formulate new hypotheses about the factors affecting the nucleation and growth of the binary superlattices. The deviation from hard sphere behavior can be explained by specific topological textures developed within deformable layers of surface ligands. Our results also suggest that the relative abundance of BNSSL phases is determined not only by their thermodynamic phase stability but also by a postulated pre-ordering of the binary fluid into local structures with icosahedral or polytetrahedral structures prior to nucleation. 

Strong electronic coupling between individual nanocrystals within a superlattice is an important prerequisite for the emergence of non-additive physical properties. However, a simultaneous realization of strong electronic coupling and dense ordered packing of nanocrystal solids has remained elusive. We report a method for growing all-inorganic highly ordered solids of electrostatically-stabilized nanocrystals with the interstitial space filled with a glassy metal chalcogenide matrix which, combined with the short separation between particles leads to very strong electronic coupling. Temperature-dependent conductivity measurements show metallic transport across our supercrystals. The formation of strongly-coupled all-inorganic nanocrystal assemblies represents an important step toward the bottom-up design of functional nanostructured composites.

2:00 PM *CP02.02.02

**Multicomponent Nanocrystal Self-Assembly for the Creation of Multifunctional Materials and Devices**

Christopher Murray1, 2; Jennifer D. Lee1; Natalie Gogotsi2; Katherine C. Elbert1; Austin A. Keller1; Daniel J. Rosen1; Chenjie Zeng1; Prashant Ramesh2 and Jungmi Park1; Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 1Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Monodisperse shape-controlled nanocrystals (NCs) are ideal building blocks for the assembly of new thin films and devices. These NCs can be thought of as "artificial atoms" with tunable electronic, optical, magnetic properties that are allowing the development of a new periodic table for design at the mesoscale. In this talk, I will briefly outline the current state of the art in synthesis, and integration of multiple NC phases and core-shell (heterostructures) NCs emphasizing the design of semiconductor building blocks with tunable shapes (spheres, rods, cubes, discs, octahedra, etc... I will then share how these tailored NCs can be directed to assemble into single-component, binary, ternary NC superlattices providing a scalable route to the production of multi-functional thin films. The in situ studies of NC organization and transformation will be carried out using a combination of X-ray scattering and electron microscopy/tomography. The modular assembly of these NCs allows the desirable features of the underlying quantum phenomena to be retained and enhanced even as the interactions between the NCs allow new delocalized properties to emerge. Synergies in electronic, optical coupling between NCs will be emphasized as we push toward the realization of artificial solids with a new 3D and structure and high mobility device integration. I will share specific case studies in thin film transistors, thermo-electric materials and solution-processable photovoltaic devices build with these strongly coupled nanocrystal solids highlighting the recent developments in wafer scale NC superlattice design and patterning may provide a path to scalable fabrication. In a final example of hetero-integration, I will present our progress in the co-assembly of plasmonic resonators together with nanoscale emitters as a route to the scalable self-assembled MetaMaterials with novel linear and non-linear optical properties. Progress toward the design of micron-sized 3D superlattice composed NC building blocks will also be shared.

2:30 PM *CP02.02.03

**Prescribing Self-Assembly of Nanoscale Architectures Through Valence Control**

Oleg Gang1, 2; Columbia University, New York, New York, United States; 2Brookhaven National Laboratory, Upton, New York, United States.

The challenges of creating designed materials via self-assembly of nanoscale blocks require establishing robust yet highly tailorable methods for directing nanoscale interactions. While it has been recognized that anisotropic bonds allow for the coordination control and, consequently, for the regulation of formed structures, the development of practical realizations was notoriously difficult. We have developed an assembly platform that through a regulation of nano-object valence allows to design a coordination symmetry. That approach permits an assembly of prescribed nanoscale architectures and complex lattices. Moreover, a variety of nano-object types can be integrated into these self-assembled hetero-architectures. This new assembly methodology requires direct 3D nanoscale visualizations, both in-situ and ex-situ, in order to probe the imperfections, a structure formation and assembly pathways. Our advances in the development of suitable x-ray- and electron- based methods for 3D characterizations will be also discussed.

3:00 PM BREAK

3:30 PM *CP02.02.04

**Polymer Nanoreactors—Vehicles to Control and Observe Nanoparticle Formation**

Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

Polymer nanoreactors have novel chemical and physical properties, which make them promising for a wide range of fields spanning catalysis, plasmonics, and electronics. However, the combinations of elements that have thus far been studied in these systems are limited by a lack of methods for preparing and analyzing multiplexed nanoparticle systems. To explore the vast number of elemental and structural combinations possible, we developed scanning probe block copolymer lithography (SPBCL), a method for synthesizing polyelemental nanoparticle arrays from polymer nanoreactors that contain metal precursors in defined amounts and ratios. Through heat treatments or electron irradiation, small nanoparticles nucleate, grow, and coarsen inside each nanoreactor eventually resulting in a single nanoparticle. The structure and formation of these spatially encoded nanoparticles can be studied using electron microscopy, both in situ and ex situ, as a function of their composition and thermal treatment. Although metal species aggregate at different rates, the final structures of the nanoparticles attain thermodynamic equilibrium. Additionally, by utilizing the fluidic polymer nanoreactors as windowless liquid "cells," the motion and interaction of ~1 nm nanoparticles during electron beam-induced solvent evaporation can be tracked in real time using an electron microscope. Taken together, SPBCL serves as a novel method for synthesizing polyelemental nanoreactors in a combinatorial manner, and the polymer nanoreactors provide a versatile platform for studying the structural evolution and final structure of complex, polyelemental systems.

4:00 PM *CP02.02.05

**Peering into the Self- and Directed-Assembly of Nanoparticles**

Hongyou Fan; University of New Mexico/Sandia National Laboratories, Albuquerque, New Mexico, United States.

Self-assembly of synthetic nanocrystals enables the positioning of nanoparticles into one to three dimensional ordered arrays, facilitating integration of nanoparticle lattices into nanophotonic and nanoelectronic architectures. The functional properties of these particle materials are expected to be highly sensitive to structural factors such as coordination number, degree of long-range order, or nanoparticle separation distance, requiring the development of robust self- and directed-assembly pathways for precise control of structural parameters to improve optical and electronic properties of functional nanoparticles. In this presentation, I will review our past efforts in development of self-assembled nanoparticles thin film arrays and in situ structural evolution at ambient conditions extend my presentation to our recent progress in development of a new Stress-Induced Fabrication method in which we applied high pressure or stress to nanoparticle arrays to induce structural phase transition and to consolidate new nanomaterials with precisely controlled structures and tunable properties. By manipulating nanoparticle coupling through external pressure, a reversible change in their assemblies and properties can be achieved and demonstrated. In addition, over a certain threshold, the external pressure will force these nanoparticles into contact, thereby allowing the formation and consolidation of one- to three-dimensional nanostructures. Through stress induced nanoparticle assembly, materials engineering and synthesis become remarkably flexible without relying on traditional crystallization process where atoms/ions are locked in a specific crystal structure. Therefore, morphology or architecture can be readily tuned to produce
System-Level Control of Structural Hierarchy in Nanoparticle Superlattices

Supramolecular chemistry is an ideal means to dynamically program structural hierarchy in both polymer and composite materials, as it uses reversible interactions between atomically precise building blocks to create well-defined nano- to macroscopic structures. Simple synthetic adjustments in molecular composition can alter how polymers bind to one another in three-dimensional space, and this in turn can modulate the nanoscale morphology of the assembled material. Conversely, once assembled, these larger-scale structures can act as scaffolds that allow multiple supramolecular binders to behave as a collective unit. Because the shape of these larger length scale motifs can affect the ability of individual supramolecular motifs or polymer chains to coordinate their binding, material form at the nanoscale could potentially be used as a design handle to tune the supramolecular groups’ collective behavior. Understanding how to holistically control structural hierarchy in this manner therefore necessitates the development of a synthetic building block whose nanoscale morphology can be tuned without significantly altering the chemical structure of the individual supramolecular binding groups themselves.

We have recently demonstrated a new polymer brush-particle building block capable of directed assembly via complementary hydrogen bonding motifs, called the Nanocomposite Tecton (NCT). NCTs consist of an inorganic nanoparticle core coated with a dense polymer brush, where each polymer chain terminates in a supramolecular bonding group; interparticle interactions drive particle assembly by creating dynamic nanoscale bonds consisting of multiple supramolecular linkages. NCT assembly is distinct from other materials synthesis methods reliant on paired hydrogen bonding motifs, as each NCT-NCT connection consists of multiple supramolecular interactions that behave collectively not because individual groups are closely linked via covalent bonds, but rather because they are geometrically confined to a localized volume at the NCT surface. An NCT’s nanoscale geometry (as dictated by the particle core size, polymer length, and polymer morphology) therefore has a strong influence on its assembly behavior, and can be used to tune NCT-NCT bond strength without changing molecule-molecule bond strength. Here we show how nanoscale structure can be used to manipulate material morphology in a holistic manner, where structural features at the molecular, nano, and mesoscopic length scales influence one another in a programmable manner, and each can be used to dictate material behavior.

SESSION CP02.03: Poster Session: Liquid-Phase TEM and Assembly
Session Chairs: Qian Chen, Liang Hong, Jianbo Wu and Xingchen Ye
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

CP02.03.01
Synthesis of Cs-Pb-Br Colloidal Crystals
Liang Zhou, Ling-Dong Sun and Chun-Hua Yan; College of Chemistry and Molecular Engineering, Peking University, Beijing, China.

Owing to their unique collective properties, colloidal crystals are attracting more and more attention. They offer us a novel method to fabricate functional materials. Nucleation and growth processes are two key factors for us to obtain colloidal crystals. Here, by changing the reaction temperature, we realized precise control of nucleation and growth rates of colloidal crystals. For the saturated solution of Cs-Pb-Br nanoparticles, a relevantly fast cooling led to nucleation of colloidal crystals, and then a very slow cooling was applied to grow colloidal crystals. Through this method, we acquired ordered cubic colloidal crystals, which was made up of 10 nm cubic Cs-Pb-Br nanoparticles. The size of those uniform colloidal crystals was about 2 μm. We found out that precursors concentration, solvents, which would influence the nucleation and growth processes, had a great influence on the final product. Through time sequence experiment, we briefly described the growth dynamics of colloidal crystal, and built the relationship between quality of colloidal crystals and nucleation/growth rates.

CP02.03.02
Observation of Carbon Nanotube Diameter via Metal Catalysts and Precursor Ratios on Carbon Foam Substrates
Nicholas Roskopf, Fabian E. Villalobos and Pedro A. Pena; Chemistry, University of California, Riverside, Riverside, California, United States.

Polyacrylilde derived carbon foams/sponges were synthesized via oxidation of simple sugars by metal nitrates leading to embedded metal particles within the carbon foam. Ni and Co in three different sugar (Xylose) to metal concentrations (20:1, 200:1, 2000:1) were varied to produce metal particles of different sizes. Carbon nanotubes (CNTs) were then grown on these carbon foams using metal catalysts, both which have favorable carbon solubility properties, as catalytic substrates. Using two different metals, and three different precursor concentrations, undergoing the same synthesis process allows for six comparable CNT diameters. Deviations in particle size and therefore CNT diameter may be a result of differences in carbon solubility, precursor concentration, among other controlled variables such as processing temperature and time. SEM micrographs allow for accurate measurement of CNT diameters and sufficient sample size for statistical analysis to reliably identify significant trends in CNT sizes based off varying metal substrates and substrate concentrations. This data may provide insight into control of CNT diameters in addition to properties such as chirality towards applications pertaining to capacitors, gas sensors, hydrophobic or oleophilic coatings.

CP02.03.03
Solution Phase Behavior of Polymer-Grafted Nanoparticles—Improving Assembly and Processability
Sarah N. Izor1,4, Tony Dagher1, Chris Grabowski1, Ali Jawaid1,4, Kyoungwoen Park1, Larry F. Drummy4 and Richard A. Vaia1, 4; 1USC, Inc., Dayton, Ohio, United States; 2Duke University, Durham, North Carolina, United States; 3SABIC, Selkirk, New York, United States; 4Air Force Research Laboratory, Dayton, Ohio, United States.

Self-assembling polymer-grafted nanoparticles (PGNs) are advancing roll-to-roll manufacturing of photovoltaics, microsystems, optoelectronics, memory, and multifunctional coatings. Architectural features of the polymeric canopy (e.g. grafting density, chain length) not only determine processability and assembly, but also robustness, such as mechanical toughness and dielectric breakdown strength. To control PGN assembly, and therefore tailor properties, a detailed understanding of solution phase behavior is imperative. However, while phase properties of macromolecules have been extensively explored, comparable knowledge of PGN solution phase behavior is lacking and fails to elucidate the role of the PGN constituents. Here we map the phase space of polystyrene-grafted gold-nanoparticles in cyclohexane by establishing the upper critical solution coexistence curve via UV-vis spectroscopy, dynamic light scattering, and small angle X-ray scattering. Increasing the molecular weight of the polystyrene graft (20 → 50 kDa) advances the coexistence curve to higher temperatures (T_C ~ 12 → 20 °C @ 10 nM (φ ~3e-5)) and increases the estimated theta temperature (θ ~ 25 → 27 °C). Considering the well-established phase behaviors of structured macromolecules, the coexistence curves and theta temperatures of PGNs are less than those of polystyrene stars (θ ~ 30 °C) and linear chains (θ ~ 33 °C). Using a TEM solution cell the impact of the proximity to the coexistence curve (e.g. spinodal decomposition θ. nucleation and growth) on the assembly process is demonstrated. Such insight refines processing techniques for slot-die coating techniques, allowing for rapid self-assembly of large-area ordered PGN monolayers directly on solid substrates.
8:00 AM CP02.04.01

New Generation Liquid Cell for Controllable Electrochemistry Experiment in the Transmission Electron Microscope
We present the design and development of a MEMS (Micro ElectroMechanical System)-based liquid cell that enables in-situ liquid electrochemistry inside the TEM (Transmission Electron Microscope). The presented device, referred to as the Nano-Cell, enables the user to work in liquid conditions with a three-electrode configuration (i.e. reference, working and counter electrodes) in order to trigger and measure chemical reactions as a function of an electrical stimulus. The design of the Nano-Cell has been done in such a way that a thin liquid layer (to minimize electron scattering and maximize resolution) is guaranteed. Furthermore, the patented on-chip inlet and outlet combined with the design of the fluidic channel offer unrivalled control of the liquid flow. As a result, the complete system gives new insights on materials characterization at the nanoscale with applications in corrosion, Lithium batteries, electroplating and materials science.
Here, we present results showing good agreement between experimental cyclic voltammetry of Ferrocenemethanol, a one-electron redox molecule in an aqueous solution and finite element modeling, allowing to characterize mass transport to the electrode and to extract reaction rates and other material properties. We demonstrate the superior fluid flow control through the MEMS based microfluidic channel. Using a pressure-based pump, both the pressure and the flow can be accurately controlled in the sample area. The resulting liquid layer thickness, in hundreds of nanometers, allows to maximize spatial resolution in TEM: while diffusion is impeded by this thin liquid layer, it mimics diffusion-limited mass transport observed in classical macroscopic electrochemistry. With additional controlled fluid flow, faster mass transport can be achieved in a similar way to other classical approaches using a rotating disc electrode or a flow cell, showing the relevance of this approach. Finally, we demonstrate experimentally controlled flow and increased mass transport to the electrode and its influence in tuning electrodeposition of copper crystals.

8:15 AM CP02.04.02

Watching Nanoparticle Growth with Tandem Self-Assembly of Nanocrystals in Solution—Insights from Real Time Analysis and Interpretation of Au Nanoparticle Self-Assembly and Its Driving Sources
Jinhui Tao; Department of Chemistry & Biochemistry, Northern Illinois University, DeKalb, Illinois, United States; 1,X-Ray Science Division, Argonne National Laboratory, Lemont, Illinois, United States.
Nanoparticles have been used in a variety of applications such as catalysts, pharmaceuticals and sensors. Controlling their growth and assembling them into a hierarchical structure is critical for the application. Current understanding of the nanoparticle growth and its assembly is mainly derived from their post-synthesis characterization. An atomic level understanding of the mechanism of nanoparticle formation and assembly during the synthesis process will be interesting and important. Tandem in-situ small angle X-ray scattering (SAXS) X-ray Absorption Spectroscopy (XAS) will be a unique way to achieve this goal. In this presentation, I will discuss the growth of nanoparticles using SAXS-XAS.

8:30 AM CP02.04.03

Real Time Analysis and Interpretation of An Nanoparticle Self-Assembly and Its Driving Sources
Jaewon Lee, Elias Nakouzzi, Miao Song, Bin Wang, Jaehun Chun and Dongheng Li; Pacific Northwest National Laboratory, Richland, Washington, United States.
The self-assembly of nanoparticles (NPs) into superlattice structures attracts great attention due to their unique optical, thermoelectric, magnetic, energy storage and catalytic properties. Understanding of and mechanisms of particle assembly and interaction between active species can help to establish conditions to control the assembly process and superlattice structure, which are closely tied to the physical and chemical properties. However, little is known about the driving forces and controlling factors during the process of particle self-assembly. In this work, we analyzed dynamic information of the process and investigated the Van der Waals force, Brownian force, and the hydrodynamic force, based on measured particle positions and velocities by directly observing the process of 2-dimensional self-assembly of nanoparticles and tracking individual particles as a function of time via in situ TEM. In addition, we studied the steric hindrance factor between particles due to the polymer attached on particle surface. We estimated the most stable conditions based on our calculations and measurements of all process self-assembly during the nanoparticle process. Experimentally, we analyzed and simulated the process of all self-assembly using in situ analysis of particle assembly.

9:00 AM CP02.04.04

Probing Crystallographic Evolution of Gibbsite Nanocrystals Using In Situ High-Field 27Al NMR Spectroscopy
Xin Zhang1, Ying Chen1, Jianzhi Hu1, Nancy Washton1, Carolyn I. Pearce1, Katharine Page1, Zhenming Wang1, James J. De Yoreo1, Sue Clark1,2 and Kevin Rosso1; Pacific Northwest National Laboratory, Richland, Washington, United States; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Washington State University, Pullman, Washington, United States.
Gibbsite (α-Al(OH)3) is important hydrosilicate of aluminum in nature that also play diverse roles across a plethora of industrial applications. In addition, it’s prominent component in high-level nuclear waste stored in large quantities at the Hanford Site, Washington and at the Savannah River Site, South Carolina. Future processing of these waste materials depends on an understanding of the behavior gibbsite crystalization, dissolution, and transformation. As a consequence, precise synthesis of the gibbsite nanocrystals with controlled particle size, shape and properties is important. Mechanisms of crystalization of gibbsite nanocrystals still remain poorly understood, particularly in complex industrial systems, which can include concentrated sodium hydroxide at low water activity. In this work, in situ magic angle spinning nuclear magnetic resonance (MAS-NMR) combine with high resolution atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman, and X-ray Pair Distribution Function (PDF) techniques were conducted to investigate the crystalization of gibbsite nanocrystals from amorphous aluminum hydroxide gel precursors and also aluminum (II) based cluster solutions. By focusing on the dynamics of aluminum coordination change from tetrahedral in solution or clusters to octahedral in solids, and the intermediate pentacoordinate state, some unifying principles governing these transformation emerge, which are important for controlling morphology of gibbsite, and management of nuclear waste.

9:15 AM CP02.04.05

Self-Assembly of Nanocrystals in Solution—Insights from In Situ Electron Microscopy
Eli Sutter; University of Nebraska–Lincoln, Lincoln, Nebraska, United States.
Solution-phase self-assembly of nanocrystals into mesoscale structures is a promising strategy for creating functional materials from nanoscale building blocks. Liquid environments are key to self-assembly since they allow suspended nanocrystals to diffuse and interact freely, but they also complicate experiments. Existing approaches for studying self-assembly have until recently been limited to assessing the final product ex-situ, or tracking long-range order in-situ in solution by reciprocal space methods. In-situ liquid electron microscopy is the only technique that provides access to real-space dynamics, especially at small scale, and is capable of probing self-assembly processes in real space in the native liquid environment. Here I will illustrate the power of in-situ liquid-cell electron microscopy to probe self-assembly of nanocrystals in solution from monomers to extended assemblies with nanometer scale resolution, and extracting fundamental information on assembly pathways and forces. Examples include self-assembly of polyhedral nanoparticles and highly anisotropic nanocrystals controlled by non-specific interactions, and programmable crystallization of DNA-nanoparticle conjugates and their real-time reconfiguration in response to external stimuli. Our results demonstrate that real-time electron microscopy can advance our understanding of solution phase self-assembly processes as a basis for designing materials with tailored functionality.

9:45 AM CP02.04.06

Interfacially-Driven Nanoparticle Nucleation Biases Hematite Crystallization Towards Oriented Attachment
Guomin Zhu1,2, Maria Sushko2, John Loring2, Jennifer Solits2, Jinhui Tao2, Benjamin Legg3, Chongmin N. Wang3 and James J. De Yoreo3,4; 1University of Washington, Seattle, Washington, United States; 2Pacific Northwest National Laboratory, Richland, Washington, United States.
Spatial and Shape Control of Soft Patches on Anisotropic Nanoparticles

A diverse class of materials exhibit characteristics of mesocrystals: single crystals composed of distinct nano-sized domains that are atomically aligned. The formation of such structures is often attributed to crystallization through oriented attachment (OA). However, many unanswered questions about the fundamental drivers and dynamic progression of this phenomenon remain. Here we focus on the crystallization of hematite (hem, Fe$_2$O$_3$) mesocrystals from ferrihydrite (fh) nanoparticles. In pure solution the resulting hem crystals can grow densely packed spherical caps, faceted plates, and core-shell structures. We investigate the effects of nucleation and assembly kinetics and addition of small molecule and polymer capping to direct the synthesis of monodisperse plasmonic NPs intimately and permanently capped with stimuli-responsive polymers. The size and shape of hairy NPs can be precisely tailored by modulating the length of inner hydrophilic block of star-like diblock copolymers. The perpetual anchoring of stimuli-responsive polymers on the NP surface captures the attractive feature of self-assembly and disassembly of NPs on demand using stimuli of different wavelengths or temperature, as revealed by tunable surface-plasmon resonance absorption of NPs and the reversible transformation of NPs between their dispersed and aggregated states. By extension, the star-like block copolymer strategy enables the crafting of a family of stable stimuli-responsive NPs (e.g., pH-sensitive polymer-capped magnetic, ferroelectric, upconversion, or semiconducting NPs) and their assemblies for fundamental research in self-assembly and crystallization kinetics of NPs as well as potential applications in optics, optoelectronics, magnetic technologies, sensory materials and devices, catalysis, nanotechnology, and biotechnology.

In the co-existing crystal and dispersed nanoparticles fluctuates due to thermal agitation, which defines the final shape of the superlattice. The tracked interface profile at the single particle resolution allows us to decompose an otherwise complicated interface into a series of Fourier components based on the capillary wave theory. Characteristics such as the interfacial stiffness at different lattice orientations and the lateral fluctuation correlation lengths are measured for the first time from real-time electron imaging. Our experiments can provide insights into the engineering the crystallization pathways and growing defect-free superlattices from solution.

To decipher the growth mechanism and quantify the kinetic parameters controlling rates, seed-free and seed system were examined in soft aqueous solution at room temperature, and the spindles grow by creation of new particles in the solution near the hm interface. Based on ATR FTIR measurements of the relative binding strength of oxalate to the (001) and (012) faces and calculations of chemical potential gradients near the interface, we propose that oxalate plays the role of inhibiting classical monomer-by-monomer growth of the hematite particles while promoting the nucleation of new hm particles at the hm/solution interface by creating a gradient in Fe$^{3+}$ chemical potential. In this way, the oxalate ligands bias the growth process away from classical mechanisms and towards oriented attachment.
Despite splendidous synthetic achievements in anisotropic nanoparticles, spatial control of their surface chemistry remains primitive. Here we demonstrate a single-pot site-specific polymer coating on anisotropic nanoparticles due to the local nanoparticle surface curvature difference. No post-coating manipulation is needed to induce the spatial patterning. Surface characterization and three-dimensional morphology of these patchy nanoparticles under scanning transmission electron microscopy and atomic force microscopy reveal the full geometry of regiospecific functionality. Mechanistic insights gained in this study via quantitative analysis on thickness, local surface curvature, and confined area on surface of patchy nanoparticles may be applicable to design hybrid anisotropic nanoparticles with directional and “soft-interaction” between themselves, which can be further expanded to bottom-up reconfigurable assembly.

SESSION CP02.05: Self-Assembly, Shape Anisotropy and Multifunction II

Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 101 B

1:30 PM *CP02.05.01
Revealing of Intermediate States During Nanocrystal Superlattice Transformations Using In Situ Liquid Phase TEM Haimei Zhong1,2; Lawrence Berkeley National Laboratory, Berkeley, California, United States; Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Nanocrystal superlattices experience structural transformations due to ligand exchange, where each individual nanocrystal acts as an artificial atom. Drastic changes of the electronic properties have been observed resulting from the superlattice transformations. For example, the electron transfer characteristics for PdSe nanocrystal superlattices are drastically different before and after PostTreatments. We report our study of PdSe superlattice structural transformations due to ligand exchange with in situ liquid cell TEM. Direct observations reveal the rare behavior of individual nanocrystals and intermediates during superlattice structural transformations. Assisted with theoretical calculations/computations, we are able to develop an understanding of the particle-particle interactions modified by ligand displacement from nanoparticle surfaces. This work also demonstrates that in situ liquid cell TEM is an indispensable approach for revealing of the pathways of superlattice transformations at the single nanoparticle level.

Acknowledgements: This work was funded by Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05CH11231 within the KC22ZHI program. The collaboration and program support through the UC Lab Fees project are also acknowledged. Dr. Yu Wang and Xinping Peng performed the in situ TEM experiments.

2:00 PM *CP02.05.02
Self-Assembly of Nanoparticle Superlattices and Their Post-Assembly Transformations Rafal Klajn, Weizmann Institute of Science, Rehovot, Israel.

Self-assembly of nanoparticles has been used to fabricate structurally diverse colloidal crystals, including binary, ternary, and quasicyristalline superlattices, many of which were found to exhibit unanticipated optical, electronic, and catalytic properties. In this talk, I will describe how these nanoparticle superlattices can be further (post-assembly) subjected to chemical reactions and transformed into novel classes of materials. I will focus on non-close-packed nanoparticle arrays, which we created through the selective removal of one of two components comprising binary nanoparticle superlattices. I will also discuss the importance of the liquid on the structure of binary superlattices assembled at the liquid-air interface and the choice of the liquid can lead to the fabrication of superlattices featuring previously unknown types of packing of the constituent nanoparticles.

2:30 PM BREAK

3:30 PM *CP02.05.03
Visualizing Self-Assembly—From Atoms to Nanostructures Utkar Mirsaidov, National University of Singapore, Singapore, Singapore.

The assembly process of nanoparticles from individual atoms, and nanostructures from nanoparticles in solution is fundamental for materials engineering and “bottom-up” fabrication of functional nanodevices. Using dynamic in situ TEM imaging [1-3] in liquids, I will describe how inorganic and organic nanoparticles form in solution and how these nanoparticles interact with each other. First, I will discuss how phase separation of a solution containing Au ions into solute-rich and solute-poor phases leads to the formation of Au nanocrystal through a pathway that does not follow classical nucleation theory (CNT). Namely, I will show that there are multiple steps that lead to the formation of nuclei from which nanocrystal grow [4]. These steps are: 1) phase separation of the liquid solution into solute-poor and solute-rich phases, from which 2) amorphous nanoparticles which serve as a precursor for nuclei emerges. This is followed by 3) crystallization of amorphous nanoparticles into crystalline nuclei. I will show that similar is true for more complex structures such as MOFs Next, I will highlight the role of intermolecular forces between nanoparticles in solution and describe their role in the assembly of nanostructures from individual nanoparticle building blocks (bottom-up approach) [5]. Specifically, I will show how the balance between repulsive hydration force and attractive van der Waals (vdW) force results in a metastable nanoparticle-pair which promotes their subsequent attachment to each other [6]. I will also briefly discuss the effect of other interactions such as electrostatic, H-bonding [7,8], and capillary forces [9] and hydrophobic interactions [10] in the context of their effect on the nanoparticle self-assembly dynamics. These findings highlight the role of solvent-mediated physical and chemical forces in material synthesis and self-assembly of nanoparticle superlattices. Our observations also emphasize the importance of direct nanoscale observation in uncovering previously unknown intermediate states that are pivotal for synthesis and self-assembly.


4:00 PM *CP02.05.04
Transmission Electron Microscopy Investigation on Pt-Based Nanocrystals for Electrocatalysis Dong Su, Brookhaven National Laboratory, Upton, New York, United States.

For metallic electrocatalysts for energy applications, understanding of structure-performance relationship can only be built on the precise characterization on the phase, interfacial and surface structures. Advanced (scanning) transmission electron microscopy (STEM) techniques have been widely applied to investigate the structure of catalysts at atomic scale. With the help of multimodal characterization techniques, it is possible to establish a direct link from the composition and surface structure to the performance of electrocatalysis. In this talk, I will discuss the recent progresses in the Pt-based catalysts for proton exchange membrane fuel cells. The first case is on how the strain and ligand effects affect the surface electronic structure and then the overall performance. In case of PtPb/Pt(110) faceted core-shell nanoplates, the biaxial strain from PtPb to Pt may help to drastically different before and after PbCl treatments. We report our study of PbSe superlattice structural transformations due to ligand exchange with in situ liquid cell TEM. Direct observations reveal the rare behavior of individual nanocrystals and intermediates during superlattice structural transformations. Assisted with theoretical calculations/computations, we are able to develop an understanding of the particle-particle interactions modified by ligand displacement from nanoparticle surfaces. This work also demonstrates that in situ liquid cell TEM is an indispensable approach for revealing of the pathways of superlattice transformations at the single nanoparticle level.

Acknowledgements: This work was funded by Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the KC22ZHI program. The collaboration and program support through the UC Lab Fees project are also acknowledged. Dr. Yu Wang and Xinping Peng performed the in situ TEM experiments.

4:30 PM CP02.05.05
Polyomorphous Self-Assembly of Nanoarrows Chang Liu1, Qian Wang2, Binbin Luo1, Limin Qi1 and Qian Chen1; 1University of Illinois at Urbana-Champaign, Urbana, Illinois,
The shape details of nanoparticle building blocks are critical to the dynamics and packing symmetry of their self-assembly process. Using liquid-phase transmission electron microscopy, we observed dynamic assembly and transformation of arrow-shaped gold nanoparticles in multiple geometric configurations. In-situ monitoring of the individual nanoparticles shows that they follow side-to-side, face-to-face or closed packing units directed by the convex or concave shape details with different relative orientations. The aspect ratio of these nanoparticles can be precisely tuned to achieve structural complexity and tunability, which can also be illustrated by the solvent evaporation-driven self-assembly. Our study provides guidance for future works of anisotropic particle self-assembly with complex structural details to have good controls in shape-oriented interaction and to enrich the library of self-assembly structures and properties.

Liquid-liquid phase separation (LLPS) of proteins into concentrated microdroplets (also called coacervation) is a phenomenon that is increasingly recognized to occur in many biological processes, both inside and outside the cell [1]. While it has been established that LLPS can be described as a spinodal decomposition leading to demixing of an initially homogeneous protein solution, little is known about the assembly pathways by which soluble proteins aggregate into dense microdroplets. Using a recently developed technique enabling the observation of matter suspended in liquid by transmission electron microscopy (TEM), we observed how a model intrinsically disordered protein (IDP) phase-separates in liquid environment. The model protein used in these experiments is Histidine-rich Peak Proteins 2 (HBP-2), a protein present in the beak of squids that can be reconstitutively obtained [2]. Our observations reveal for the first time dynamic mechanisms by which soluble proteins self-organize into condensed microdroplets, with nano-scale and milli-second space and time resolution, respectively. With this method, and the initial and natural growth steps of the LLPS could be captured, opening the door for a deeper understanding of other biomacromolecular complexes exhibiting LLPS ability.


8:00 AM CP02.06.01
Size Dependency of the Ferroelectric Properties in Single Nanocrystals of BaTiO₃: Locally Investigated by HRTEM and PFM
Hortense Le Ferrand, Martial Duchamp, Bartosz Gabryelczyk, Cai Hao and Ali Miserez; Nanyang Technological University, Singapore, Singapore.

Despite the study of BaTiO₃: for more than a half of a century, the physical and functional properties of this material at the nanoscale are still poorly known. This is due to the presence of multiple concomitant factors that are difficult to disentangle from macroscopic experiments. One of the distinctive characteristics of BaTiO₃ is the ferroelectricity, which is associated to the coherent and collective displacement of Ti ions that give origin to an electrical charge separation at the surface. However, at reduced crystals size (tens or couple hundred of nanometers) the polar ordering of this material changes significantly from the bulk. From commonly employed experimental techniques used to study the crystal structure and phase transitions, such as XRD, Raman, DSC, and dielectric spectroscopy; the reorientation of the crystal size results in peaks broadening and higher signal to noise ratio. Therefore, the crystal structure, phase transition temperature, and polar ordering of perovskite nanocrystals at the nanoscale is still unclear. To overcome these issues, PFM and HR-STEM have been employed to study the ferroelectricity and the atomic columns displacement of single nanocrystals of BaTiO₃, with sizes of 15 nm, 30-50 nm, and 100 nm. The results demonstrated that the 100 nm nanocrystals show behavior similar to bulk BaTiO₃, with a sharp ferroelectric to paraelectric phase transition around 110 °C. By decreasing the size of the nanocrystals at around 40 nm, it has been observed from HR-STEM images that the polarization was not anymore along the [001] axis and could be either [011] or [111] direction. In support to the HR-STEM data, the PFM hysteresis loops have shown a shape variation while increasing the temperature that has reorientably obtained [2]. Our observations reveal for the first time dynamic mechanisms by which soluble proteins self-organize into condensed microdroplets, with nano-scale and milli-second space and time resolution, respectively. With this method, and the initial and natural growth steps of the LLPS could be captured, opening the door for a deeper understanding of other biomacromolecular complexes exhibiting LLPS ability.


8:15 AM CP02.06.02
Design and Characterization of Chemically and Mechanically Tunable Room-Temperature Liquid Metal Colloids Zachary Farrell1, 2, Nicholas J. Morris1, 2 and Christopher Tabor1; 1AFRL, WPAFB, Ohio, United States; 2AFRL, WPAFB, Ohio, United States.

Exeutic Gallium-Indium alloy (EGaIn), a room temperature liquid metal, is of interest for components which leverage its liquid state and rapid alloying behavior for application such as reconfigurable and self-healing electronics. Additionally, its tendency to rapidly self-passivate by production of native gallium oxide allows for simple production of EGaIn colloids which resist spontaneous recoalescence. Although EGaIn has been used in applications such as these, to date, most approaches in this area have an ad hoc character due to a lack of fundamental knowledge on the chemical and mechanical nature of the native gallium oxide and the process by which it develops. To provide insight in these areas, we demonstrate the production and functionalization of EGaIn colloids with the aim of carefully tuning the gallium oxide shell thickness and thus the derivative chemical and mechanical properties of the particles. To accomplish this, orthogonal ligand chemistries consisting of thiols or phosphonic acids are chosen to selectively bond to either elemental gallium, native gallium oxide, or both. Characterization with XPS and nanoprinting of the resultant particles shows that not only can the gallium oxide shell thickness be tuned over nearly a full order of magnitude, but the particles also show good adherence to Reissner’s scaling theory which is commonly applied to other core-shell particles. We anticipate approaches such as these to find application in devices such as self-healing electronics where fine control over particle mechanical properties is desirable to ensure a robust and reliable response to an initiating stimulus.

8:30 AM *CP02.06.03
Direct Observation of Chemical and Mechanical Nanoscale Forces Matthew R. Jones; Chemistry, Rice University, Houston, Texas, United States.

Chemical and mechanical processes occurring at nanoparticle surfaces underlie ligand binding, intraparticle ripening, and particle deformation, to name a few. The ability to directly observe the time evolution of these systems would provide unprecedented mechanistic insight to these important fundamental systems. In this work, we leverage liquid-phase transmission electron microscopy techniques to monitor the chemical and mechanical nature of noble metal nanoparticles as they respond to external stimuli. More specifically, we track molecular binding events on immobilized nanoparticle templates to reveal ligand binding preferences for certain inorganic crystal facets. In addition, we
show the ability to controllably deform single nanoparticles in response to liquid-phase stimuli and use imaging data to understand the spatiotemporal dissipation of strain in confined crystalline materials. Finally, we look at the interplay between chemistry and mechanics at the nanoscale to influence how external stimuli can drive reconfigurable nanoparticle-based materials and devices.

9:00 AM CP02.06.04 Liquid Phase Imaging of Dynamic Biological Systems—A Multifaceted Approach Madeline J. Dukes¹, A. C. Varano², William J. Deanaley² and Deborah F. Kelly³; ¹Protochips, Inc., Morrisville, North Carolina, United States; ²Virginia Tech Carilion Research Institute, Virginia Tech, Roanoke, Virginia, United States.

State-of-the-art in situ and operando transmission electron microscopy (TEM) applications have skyrocketed in recent years, permitting scientists to observe dynamic processes at the nanoscale. As the techniques evolved, so have the designs for liquid cell specimen holders. New advanced holders are capable of controlling liquid environments while simultaneously delivering external stimuli [1]. Samples encapsulated in liquid retain their freedom to move as real-time analysis provides new insights for protein aggregation, diffusion, particle interactions, and mechanistic changes [1]. Thus, researchers can gain a more complete understanding of individual systems beyond static snapshots acquired by traditional TEM methodologies.

Combining liquid-phase TEM (LP-TEM) with low-dose imaging and down-stream computational procedures provides unique quantifiable data of biological entities. Recent work to determine aggregation properties of a protein-based therapeutic reagent, PEGylated Interferon α2a, revealed diffusion and growth behaviours as a function of time [3]. Understanding these aggregation steps is beneficial for developing effective drugs with low side-affects. Such studies represent a new means to improve our understanding of aggregation dynamics under physiologically relevant conditions.

Using the same techniques, we were able to correlate the nanoscale motion of actively transcribing double-layered rotavirus particles (DLPs) with cryo-EM reconstructions. A side-by-side comparison of the two techniques showed increased internal disorder in actively transcribing DLPS versus those in a resting state (not actively transcribing). These correlative applications advance our ability to quantify molecular dynamics in the context of three-dimensional structural information.

Finally, a new exciting path for LC-TEM involves tomographic data collection of samples in liquid. In closed cell specimen holders, measurements are limited by a reduced ability to tilt the holder to higher angles. To address this issue, we developed a sandwich approach that utilizes a conventional carbon TEM grid in combination with a silicon nitride microchip having integrated microwells to enclose liquid specimens. Tomographic data from this work proved useful for microbiology studies and the technique is currently in development to monitor host-cell pathogen interactions in real-time.

Collectively, these results demonstrate the wide variety of fundamental processes that benefit from in situ and in situ-adjacent imaging strategies to visualize/cooperate biological systems that inhabit the nanoworld around us.

References:

9:30 AM CP02.06.05 Mechanistic Study of Galvanic Replacement of Chemically Heterogeneous Templates Alexander Chen, Sophia McClain and Sara Skrabalak; Indiana University, Bloomington, Indiana, United States.

Galvanic replacement is a useful method for synthesizing architecturally complex bimetallic nanomaterials from monometallic templates. The oxidation of a monometallic template by ions of a more noble metal is well studied; however, chemically heterogeneous templates offer more than one type of reaction site and potentially structurally more complex materials. Yet, mechanistic studies with such templates are limited. Here, the reactivities of Ag and Pd in Janus-style AgPd dimers are compared when Au ions capable of oxidizing both metals are introduced, revealing (1) the selectivity of an oxidant in galvanic replacement for oxidizing one of two available reductants, (2) the interaction between galvanic replacement and solid-state diffusion, and (3) the similar replacement mechanisms for different redox pairs. Specifically, when in the presence of Ag and Pd nanocrystals, Au ions with various reduction potentials and oxidation states almost exclusively replace Ag first and Pd second, and when Ag and Pd are physically joined in dimers, Ag oxidation facilitates diffusion of the remaining Ag toward the Pd domain. These results provide mechanistic insight into the kinetically linked processes involved in the galvanic replacement of complex multimetallic templates, and demonstrate the importance of understanding these interactions in order to achieve structural and compositional control over the resulting nanomaterials.

9:45 AM CP02.06.06 Synthesis and Characterisation of Calcium Carbonate-Based Nano- and Micro- Structural Materials Fearghal C. Donnelly¹, Yurii K. Gurko¹, ² and Finn Purcell-Milton¹; ¹School of Chemistry, Trinity College Dublin, Dublin, Ireland; ²School of Chemistry, ITMO University, Saint Petersburg, Russian Federation.

Calcium carbonate is a ubiquitous material, which has a high commercial importance and a variety of important applications. For example, calcium carbonate has traditionally found uses in the construction industry in the production of lime mortar and cement while its whiteness and high refractive index leads to its use in the manufacture of high-gloss paper and as a white pigment in the paint industry. In addition, CaCO₃ demonstrates excellent biocompatibility, enabling its biomedical applications such as in antacid tablets, bone regeneration and drug delivery systems.

The main goal of our work is the development of new CaCO₃ based nano- and micro-structural materials using various synthetic techniques. Here, we present our work on CO₂ bubbling, precipitation-based syntheses, and a novel dry ice carbonation method for the preparation of nano- and micro-particles of CaCO₃. CO₂ bubbling, which is the preferred method for industrial carbonation, was studied and the parameters affecting its synthesis were subsequently refined. Precipitation reactions were used to finely control the synthesis of unique CaCO₃ materials, and subsequently their chiral and luminescent properties. Finally, a unique dry ice carbonation method was developed enabling us to produce CaCO₃ morphologies which are not typically attainable using standard preparation approaches. We believe that this work will contribute to further development of CaCO₃ based materials with a range of potential applications.


10:00 AM BREAK

10:30 AM CP02.06.07 Poly(N-vinylpyrrolidone) Influences Shape-Control of Ag Nanocubes Through Reduction Kinetics Instead of Preferential Binding to Specific Facets Supriti Jharimune¹, Robert M. Rioux¹, Zhiqiang Chen¹, Rudeben Pldwa², Ji Woong Chang¹ and Bert Klumperman¹; ¹Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ²Department of Chemistry and Polymer Science, Stellenbosch University, Matieland, South Africa; ³Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States; ⁴Department of Chemical Engineering, Kumoh National Institute of Technology, Gumi-si, Korea (the Republic of).

Poly(N-vinylpyrrolidone) (PVP) is ubiquitously used in shape-controlled polyol synthesis of metal nanoparticles (NPs). Among the various systems using PVP, Ag nanocubes (NCs) synthesis has emerged as one of the most robust systems, where PVP is considered as the structure-directing agent and ethylene glycol (EG) as the reducing agent for Ag⁺ at
elevated temperature. While several reports indicate molecular weight ($M_w$) and monomer concentration ($C_m$) of PVP impact the final shape of NPs, a general consensus on the role of PVP during the synthesis of Ag NCs using polyol method is thus far lacking. Recent experimental studies from our group indicate the differential heat of adsorption of PVP to (100) versus (111) facets is too small to predict a cube over an octahedron via a thermodynamic Wulff construction. We further demonstrate that chloride (Cl$^-$) added as HCl is the structure-directing agent in synthesis of Ag NCs. However, it has been observed that PVP can impact the final shape as its $C_m$ or $M_w$ is changed, suggesting PVP may influence the rate of nucleation, leading to kinetically-preferred shapes even in the presence of Cl$^-$. We demonstrate PVP acts both as stabilizer and the dominant reducing agent in the synthesis of Ag NCs owing to displacement of the capped PVP molecules, thereby demonstrating the stabilizing role of PVP. Optimal studies of Ag$^+$ reduction at different PVP $C_m$ and $M_w$ shows faster reduction rate at higher $C_m$ for the same $M_w$ of PVP and at lower $M_w$ for the same $C_m$, suggesting PVP rather than EG plays a dominant role in the reduction of Ag$^+$ and the reducing effect originates from the end groups of PVP. We constructed an experimental phase diagram for the formation of Ag NCs by varying the PVP $C_m$ and $M_w$ at constant temperature. Between the high and the low boundaries of the phase diagram, any combination of PVP $C_m$ and $M_w$ can yield uniform Ag NCs. The lower boundary is related to a required minimum amount of PVP for stabilization, while the upper boundary is related to the role of PVP in Ag$^+$ reduction. Finally, in order to bridge the gap over existing arguments regarding the identity of end functional groups in commercial PVP (–OH or –CHO) and the functional group in PVP molecule responsible for Ag$^+$ reduction, we synthesized PVP with modifiable end-groups and a precise control over the average $M_w$ for a systematic comparative study of Ag NC synthesis. Experiments suggest end groups are indeed responsible for Ag$^+$ reduction kinetics; PVP with –OH end groups are more potent reducing agent than those with –CHO end groups. This work provides key insights into understanding the role of PVP in controlling reduction kinetics of Ag$^+$ and thereby influencing the shape of Ag NPs during polyol synthesis.

10:45 AM CP02.06.08
Study of Charge Effect on Nanoparticle Self-Assembly by Liquid Transmission Electron Microscopy

Yuzi Liu; Argonne National Laboratory, Lemont, Illinois, United States.

Self-assembly of nanoparticles into mesoscopic structures is a proposed concept in material science and technology for the fabrication of hybrid systems with collective properties for different purposes. Liquid cell TEM provides a direct imaging approach that enables to watch the movement of nanoparticles in real time. Here, it was employed to study the self-assembly process of nanoparticles with different charges to unravel the charge effect on self-assembly. It was found that the positively charged nanoparticles can assemble to quasi one dimensional structures when the electron beam intensity exceeds a threshold, while negatively charged particles do not move under the e-beam. We also found size select assembly. The high energy electron beam effect is the driven factor on the self-assembly process. The individual particles show a preference to attach to the ends of existing dimers, trimers to form trimer and tetramer. The long distance dipolar interaction and short distance Van der Waals are the dominant control interaction in the formation of anisotropic one dimensional structure. We further investigate the self-assembly of Au nanoparticles (positively charged) under biased conditions in liquid environment. The different biased voltage was applied to nanoparticle suspension. It was found that the nanoparticles start moving at certain biasing condition. By statistics, the nanoparticle displacement is roughly the same under different biased voltage. But the number of moving nanoparticles is increasing along with the higher biased voltage. We also studied the self-assembly of non-charged nanoparticles. The fractal structure was formed and the hierarchical assembly was observed.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences User Facility under Contract No. DE-AC02-06CH11357.

11:15 AM CP02.06.09
Probing Synthesis, Bandgaps and Stability of a Family of Cs₂AgMX₆ Lead-Free Double Perovskite Nanocrystals (M = Sb, Bi, In; X = Cl, Br)

Jakob Dahl; 1 Emory M. Chan; 1 and Paul Alivisatos; 1, 2 Chemistry, University of California, Berkeley, Berkeley, California, United States; 1Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Lead toxicity has sparked interest into alternative halide nanomaterials with properties similar to CsPbX₂ perovskites. A promising alternative suggested from bulk studies is the family of double perovskites of the form Cs₂AgMX₆. Here, we report the robust and tunable synthesis of colloidal nanocrystals of Cs₂AgInCl₆ and Cs₂AgSbCl₆ via injection of acyl halides into a metal acetate solution under atmospheric conditions and relatively mild temperatures. We demonstrate the synthesis of single crystalline cubic nanocrystals of Cs₂AgMX₆ for a systematic comparative study of Ag NC synthesis. Experiments suggest end groups are indeed responsible for Ag$^+$ reduction kinetics; PVP with –OH end groups are more potent reducing agent than those with –CHO end groups. This work provides key insights into understanding the role of PVP in controlling reduction kinetics of Ag$^+$ and thereby influencing the shape of Ag NPs during polyol synthesis.

11:30 AM CP02.06.10
Visualizing Electrochemical Reactions at the Nanoscale by In Situ TEM

Huolin L. Xin; 1 Ruqian Lin; 2 Mingxing Gong; 2 and Nikhilendra Singh; 1 University of California, Irvine, Irvine, California, United States; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, California, United States; 2Huazhong University of Science and Technology, Wu Han, California, United States; 2Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

Over the past five years, we have witnessed a rapid growth in liquid and gas flow holders for TEM and X-ray microscopes. These holders have enabled direct imaging of material transformations in liquid and gaseous environments with submicron-scale to atomic-scale spatial resolution. In particular, research regarding electrode materials in lithium ion batteries and nanocatalysts in heterogeneous catalysis has greatly benefited from the emergence of these capabilities. Despite their initial success in in-situ battery studies, similar transformations in liquid and gaseous environments with submicron-scale to atomic-scale spatial resolution. In particular, research regarding electrode materials in lithium ion batteries and nanocatalysts in heterogeneous catalysis has greatly benefited from the emergence of these capabilities. Despite their initial success in in-situ battery studies, similar challenges remain for the in-situ study of electrocatalysts using an operando TEM liquid holder and I will also discuss existing challenges that the in-situ EM field need to address.

SESSION CP02.07: Other Colloidal Assembly
Session Chair: Qian Chen
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 101 B

1:30 PM CP02.07.01
Self-Assembly of Anisotropic Nanocrystals

Qiu Chen; Chemistry, Brown University, Providence, Rhode Island, United States.

Anisotropic nanocrystals with defined surface patchiness represent a unique class of building objects for constructing high-order architectural nanomaterials. When utilizing in assembly, on the one hand, anisotropic nanocrystals can display strong asymmetric interactions induced by the patchiness that may complicate the formation of ordered structures compared to the assemblies of isotropic building blocks. The same asymmetric interactions, on the other hand, can not only result in novel translational orderings, but also induce correlations between the atomic orientations of HNCs upon crowding, thus possibly dictate and control the atomicic lattices within the assembled superstructure. In this talk, I will use several types of anisotropic 'patchy' nanocrystals as examples to demonstrate how they assemble into the unprecedented superstructures through the directional interactions among the building blocks under an enthalpy-driven condition. Both translational periodicities and orientational ordering of the final superstructural materials will be discussed. The dominating driving forces lead to the obtained architectures will be identified through molecular dynamics computer simulations and experimental results.

2:00 PM CP02.07.02
Assembly and Rheology of 2D Colloids and Their Role in 3D Printing

Andrew Corker; 1, 2 Henry Ng; 2, Rob Poole; 2 and Esther Garcia-Tunón; 1, 2, 3 Materials Innovation Factory, University of Liverpool, Liverpool, United Kingdom; 3School of Engineering, University of Liverpool, Liverpool, United Kingdom.

Additive manufacturing (AM) techniques have undergone enormous growth in the past couple of decades and have already revolutionised the process of rapid prototyping and
manufacture of multfunctional, complex architectures. Due their interesting structure and surface chemistry, 2D colloids can be used in additive manufacturing to create complex structures with many unique characteristics, or can be used in composite formulations for a wide range of applications including: photovoltaic electronics, flexible transparent electrodes for energy storage to water purification.

Extrusion-based 3D printing, also known as Direct Ink Writing (DIW) or robocasting, provides a unique approach to introduce advanced and high-added-value materials with limited availability into lab-scale in manufacturing. Robocasting involves continuous extrusion of colloidal pastes or gels through a fine nozzle to create 3D structures layer-by-layer. Formulation design aims to ensure “printability” through careful control of rheology. The inks or pastes must be shear thinning to easily flow through the nozzle at modest shear rates and then immediately set into a non-flowing structure once printed. They must also be able to support multiple layers on top and retain the shape across spans without deformation. “Printability” however is still a broad concept due to the diverse range of applications within the field. This work compiles different rheology methodologies combining shear, extensional and oscillatory rheology that will enable quantifying the printability of soft materials.

2D colloids of graphene oxide (GO) exhibit a fascinating rheology and can aid the processing of different materials to develop ‘printable’ formulations. GO colloids in water form printable networks at relatively low concentrations and can behave as multifunctional additives. Due to unique surface chemistry GO, can be used to act as a rheology modifier that imparts a strongly shear-thinning and yield stress (ey) to suspensions of other materials even when is used in small concentrations. This work provides an in-depth rheological study of GO suspensions with a wide range of behaviours from Newtonian-like to viscoelastic ‘printable’ soft solids. The combination of extensional shear rheology reveals the network formation process as GO concentration increases from <0.1 vol% to 3 vol%. Results from the extensional tests showed how the GO transitions from a Newtonian-like liquid (<0.1vol%) to weakly (<0.8vol%) and then strongly-established structural network as concentration is increased. Our results also demonstrate that the quantification of ‘printability’ can be based on three rheology parameters: the stiffness of the network via the storage modulus (G’), the solid-to-liquid transition or flow stress (σf), and the flow transition index, which relates the flow and yield stresses (FTI=σf/ey).

2:15 PM CP02.07.03 Self-Assembly of Non-Spherical Nanoparticles into Functional Supercrystals Zewei Quan*; Chemistry, Southern University of Science and Technology, Shenzhen, China.

Nanoparticles are fascinating in many ways. Self-assembly of various building blocks into macroscopic structures with desired features and functions, is an interesting theme that runs through chemistry, biology and material science. In this talk, I will first show our recent progress in the self-assembly of non-spherical nanoparticles including nanocubes, nanorods, and nanodumbbells. The roles of non-spherical nanoparticle shape during this self-assembly behavior are of great interest, and different solvents have been demonstrated to modulate the individual particle interactions to control the final nanoparticle assembly pattern. Additionally, the stability of different nanoparticle superlattice polymorphs has also been provided with dedicated solution calorimetric measurements. Last, I will talk about how to use self-assembly technique to prepare ordered Au mesoporous nanosheets with plasmonic hotspots.

References:

2:30 PM CP02.07.04 Direct-Write Freeform Colloidal Assembly Alvin Tan, Justin Beroz, Mathias Kolle and A. John Hart; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Assemblies of colloidal particles exhibit complex collective behaviors based on particle geometry, composition and arrangement, which enables tailored design of novel materials for diverse applications. Methods to deposit and self-assemble ordered particle solids from suspension are typically limited to fabrication of films and patterns, and commonly utilize surface tension to confine particles against substrates. In contrast, direct-write methods to build 3D structures rely on cohesion between particles in high-density suspensions to achieve structural rigidity, but this precludes particle ordering. Here, we present a method to build freestanding structures from self-assembled colloidal particles. The structures have mm-cm scale dimensions and can be built in freeform with aspect ratios greater than 10, yet retain polycrystalline order. We derive a scaling law that governs the rate of assembly, show how macroscopic structural color can be tailored via the size and crystalline ordering of polystyrene particles, and build exemplary freestanding functional structures. Owing to the diversity of colloidal building blocks and means to control their interactions, direct-write assembly could therefore enable novel composites, photonics, electronics, and other materials and devices.

2:45 PM CP02.07.05 Colloidal Crystals Engineered from Anisotropic Nanoparticles and DNA Haixin Lin, Lin Sun, Jinghan Zhu and Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

DNA-mediated programmable assembly is a promising route for synthesizing novel materials. This strategy has been successfully used to synthesize crystalline structures with more than 35 different symmetries and over 500 structures. However, most of the properties of these colloidal crystals are dictated by the identity of the building blocks, instead of their structural arrangements. In contrast, crystal structure plays a crucial role in determining the properties of several traditional molecular/atomic crystals such as porous (e.g. MOFs, clathrates, zeolites) and anisotropic crystals (e.g. uniaxial crystals, biaxial crystals). Analogous porous or anisotropic colloidal crystals are difficult to fabricate given that the most commonly used building blocks are highly symmetric spherical particles. Unlike spherical particles, anisotropic particles can directionally guide the formation of DNA bonds with specific angles, which affects the lattice symmetry and crystal habit of the resulting colloidal crystals. In this work, we show two examples of how low symmetry nanoparticles assemble into either porous or anisotropic crystals.

3:00 PM BREAK

SESSION CP02.08: Nanoparticle Application
Session Chair: Qian Chen
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 101 B

3:30 PM CP02.08.01 Superhydrophilic Wrinkle-Free Cotton Fabrics via Plasma and Nanofluid Treatment Lihong Lao, Liling Fu, Genggeng Qi, Jintu Fan and Emmanuel P. Giannelis; Cornell...
For more than two decades in the apparel industry, there has been a consistently high demand for wrinkle-free cotton garments for easy care and comfort. Conventional wrinkle-free finishing is based on the crosslinking reaction between molecular chains of cellulose via formaldehyde derivatives such as dimethyldihydroxyethyleneurea (DMDHEU).

DMDHEU introduces hydroxyl (-OH) groups in cotton, which increases wrinkle-resistance and shape retention. However, the finishing reduces the hydrophilicity of the fabric due to the reduction of the number of OH groups; consequently, the moisture sorption capacity and wicking properties are reduced, resulting in a deterioration in the comfort of the cotton fabric. Therefore, recovering the hydrophilicity of wrinkle-free finished cotton has very significant practical value.

We demonstrate in this study, a wrinkle-free, superhydrophilic, cotton fabric (contact angle 0°) by attaching specially engineered nanoparticles to plasma pre-treated cotton fabric. Because of their charged nature, the nanoparticles are firmly anchored on the fabric via electrostatic interactions; the surface structures were confirmed by image and chemical analyses. The durability of wetting behavior and wrinkle-free property of the NP-coated fabric was evaluated via aging, laundering and abrasion tests. The strongly attached coatings are stable maintaining their superhydrophilic nature even after 60 days’ aging and 50 laundering cycles. The nanoparticle-coated fabric also combines superhydrophilicity with very good wrinkle-recovery property, tensile strength and abrasion resistance (25,000 abrasion cycles) performance.

3:45 PM CP02.08.02
High Performance Unpoled Piezoelectric Device Comprised of Surface Modified 3D Li-ZnO into PVDF Polymer Incorporated with MWCNT Aminur Rashid Chowdhury, Jared Jaksic, Istita Hussain, Phong Tran and Jasmir M. Uddin; The University of Texas at Rio Grande Valley, Edinburg, Texas, United States.

In last few years piezoelectric materials have found its position as one of the leading stress sensing element in real life applications. Hence the demand for developing highly effective and sensitive piezoelectric devices is the all-time high. We present an unpoled high performance flexible piezoelectric nanogenerator comprising of three-dimensional(3D) surface modified Lithium doped Zinc Oxide (Li-ZnO) with Multwallared carbon nanotube (MWCNT) in bulk matrix of Polyvinylfluoride (PVDF). 3D Li-ZnO was synthesized hydrothermally followed by surface modification by polyethylene glycol (PEG-20000). The polyethylene glycol coating served as an effective solution for avoiding electrical poling and enhanced the proportion of the PVDF β-phase while MWCNTs acted to increase conductivity and to reinforce the composite during mechanical stressing. This also acted as a cost-effective multifunctional piezoelectric device. The piezoelectric nanocomposite was tested with different body motions to assess this piezoelectric device's efficiency in real-world application. The piezoelectric device was found with promising a linear response to a gradual increase in normal stresses. This device also shows a promising use for biomedicine as PVDF, ZnO is FDA approved.

4:00 PM CP02.08.03
Chirality Inversion on the Carbon Dot Surface via Covalent Surface Conjugation of Cyclic α-Amino Acid Capping Agents Fatemeh Ostadhossein, Gururaja Vulpugundam, Santosh Misra, Indrajit Srivastava and Dipanjnan Pan; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Manipulating the chiroptical at the nanoscale is of great importance in stereoelectronic reactions, enantioseparation, self assembly and biological phenomena. In recent years, carbon dots have garnered great attention due to their favorable properties such as tunable fluorescence, high biocompatibility, and facile, scalable synthetic procedures. Herein, we report for the first time the unusual behavior of cyclic amino acids due to the surface of carbon dots prepared via microwave-based carbonization. Various amino acids were introduced on the surface of carbon dots via EDC; NHS conjugation at room temperature. Circular dichroism results revealed that although most of the surface conjugated amino acids can preserve their chirality on negatively charged, ‘bare’ carbon dots, the ‘handedness’ of cyclic α-amino acids can be flipped when covalently attached on carbon dots. Moreover, these chiral carbon dots were found to interact with the cellular membrane or its mimic in a highly selective manner due to their acquired asymmetric selectivity. Comprehensive inhibitor study was conducted to investigate the pathway of cellular trafficking of these carbon dots. Overall, it was concluded that chirality of amino acid on the surface of carbon dots could regulate many of the cellular processes.

4:15 PM CP02.08.04
Colloidal Cs\textsubscript{x}FAP\textsubscript{1-x}\textsubscript{A}\textsubscript{B}\textsubscript{x}\textsubscript{X}\textsubscript{1-x} Perovskite Nanocrystals with Full Range of A-Site Composition Tuning for High Voc Solar Cells Abhijit Hazarika\textsuperscript{1}, Qian Zhao\textsuperscript{1, 2}, Ashley Gaulding\textsuperscript{1, 3}, Jeffrey Christian\textsuperscript{1}, Benjia Dou\textsuperscript{1, 3}, Ashley Marshall\textsuperscript{1}, Taylor Moot\textsuperscript{1}, Joseph Berry\textsuperscript{1}, Justin Johnson\textsuperscript{1} and Joseph Luther\textsuperscript{1}; National Renewable Energy Laboratory, Lakewood, Colorado, United States; \textsuperscript{2}College of Chemistry, Nankai University, Tianjin, China; \textsuperscript{3}University of Colorado Boulder, Boulder, Colorado, United States.

Due to their amazing optoelectronic properties, colloidal lead halide perovskite nanocrystals (NCs) are receiving increasing attention in recent times. Perovskite NCs possess properties that are not accessible in their bulk or thin-film counterparts. For example, perovskite phase of CsPbI\textsubscript{3} is unstable in ambient condition in bulk or thin-film, but they are phase stable in their quantum confined form. This particular material has shown to have record efficiency for quantum dot (QD) solar cells. Another interesting advantage of these QD materials is that their compositions can be tuned without changing the crystal framework either by direct synthesis or by post-synthetic ion exchanges. Particularly, X-site ion exchange in the perovskite NCs with general formula A\textsubscript{x}B\textsubscript{1-x}FAP\textsubscript{x} can be achieved both in QDs and thin films, and it has been shown that only compositions with 1-x<0.4 can be realized in the pure usable perovskite phase. This is due to thermal instability of FAPbI\textsubscript{3} (crystallizes at around 130 °C) at temperatures required to crystallize CsPbI\textsubscript{3} (above 300 °C). Here, we present a simple post-synthetic cross-cation exchange reaction between colloidal solutions of CsFAPbI\textsubscript{1-x} and FAPbI\textsubscript{x} nanocrystals just by mixing them at temperatures slightly above the room temperature that enables us to achieve compositions in the whole range of 0<x<1. This helps us to realize compositions that were not known previously. The photoluminescence (PL) kinetics studies reveal that the activation energy required to inter-exchange the Cs\textsuperscript{+} and FA\textsuperscript{−} ions is around 0.65 eV, higher than that for X-site exchange in lead halide perovskites. We use these alloyed colloidal perovskite quantum dots to fabricate photovoltaic devices. We applied these alloyed NC ink in solar cell and demonstrated that they exhibited high open circuit voltage (V\textsubscript{OC}) of ~90% of their Shockley-Quiesser maximum and have lower losses than the thin film perovskite devices of similar compositions.

References
6. Abhijit Hazarika, Qian Zhao, E. Ashley Gauldlin, Jeffrey A. Christians, Benjia Dou, Ashley R. Marshall, Taylor Moot, Joseph J. Berry, Justin C. Johnson, and Joseph M. Luther, ACS Nano, 2018, 12 (10), 10327.

4:30 PM CP02.08.05
Tuning the Optical Properties of Pulsed Laser Synthesized Nitrogen Doped Graphene Quantum Dots Muhammad Shehzad Sultan\textsuperscript{1}, Vladimir I. Makarov\textsuperscript{1}, Muhammad Sagjad\textsuperscript{1}, Frank Mendoza\textsuperscript{2}, Wojciech M. Jadwisiencka\textsuperscript{2}, Brad R. Weiner\textsuperscript{1} and Gerardo Morell\textsuperscript{1}; \textsuperscript{1}Department of Physics, University of Puerto Rico, San Juan, Puerto Rico, United States; \textsuperscript{2}Department of Physics and Astronomy, Austin Peay State University, Austin, Tennessee, United States.

The graphene quantum dots (GQDs) have attracted the attention of researchers due to their excellent properties and potential applications in biomedicines, energy storage devices and photocatalysts. Photoluminescence is one of the most important characteristics of GQDs. The doping of GQDs with Nitrogen atoms is one of the most effective ways to tune their photoluminescence emission and to increase quantum yield. In this work, high-quality Nitrogen-doped graphene quantum dots (N-GQDs) were synthesized by using pulsed laser synthesis method at various irradiation powers of pulsed laser and changing the concentration of nitrogen doping to effectively tune the photoluminescence emission and improve the quantum yield (QY) of as synthesized N-GQDs. The TEM, HRTEM, XPS, XRD, Raman spectroscopy and FTIR were carried out to observe the morphology, size distribution, crystalline structure and to prove successful doping of GQDs with nitrogen atoms. To observe optical properties of as synthesized N-GQDs, the UV-vis and Photoluminescence measurements were carried out. The as-synthesized N-GQDs exhibit high quality crystalline structure of graphene. A high quantum yield was exhibited by the obtained N-GQDs as compare to the pristine GQDs. The obtained N-GQDs with oxygen-rich functional groups exhibit a strong emission. This work may be helpful to expand the
In this presentation, we will describe the colloidal synthesis of phase-pure nanocrystals (NCs) of a highly abundant mineral, chalcopyrite (CuFeS₂). The steady state optical extinction spectrum of these NCs offers few surprises due to Fe which introduces deep energy levels in the electronic band structure, as supported by our density functional theory (DFT) calculations. The spectrum is characterized by absorption bands centered at around 480 and 930 nm, spanning almost the entire visible and near infrared regions. These are ascribable to electronic transitions from the valence band (VB) to the empty intermediate band (IB), located in the so-called fundamental band-gap and composed predominantly of Fe 3d orbitals. We further demonstrate, through spectroscopic measurements and ab initio calculations that these NCs actually sustain metal-like quasi-static optical resonances despite the absence of free carriers in the NC ground state owing to this unique band structure. Laser-irradiation (at 808 nm) of an aqueous suspension of these CuFeS₂ NCs exhibited significant heating, with a photothermal conversion efficiency of 49%. Such efficient heating is most likely due to the carrier relaxation within the broad IB band, as corroborated by transient absorption measurements and further described by DFT calculations. The intense absorption and high photothermal transduction efficiency (PTE) of these NCs in the so-called biological window (650–900 nm) make them suitable for photothermal therapy as demonstrated by tumor cell annihilation upon laser irradiation. We intend to put forward the chemistry behind the synthesis of these low band-gap ternary semiconductor NCs and describe the optoelectronic properties using experimental and theoretical points of view, through this presentation. A suite of spectroscopic techniques, which include visible-infrared transient absorption, x-ray absorption and emission, resonant inelastic x-ray scattering (RIXS) were used in our analyses. The subsequent use as a photothermal agent is an offshoot of this understanding. The presence of the deep Fe levels constituting the IB is the origin of such enhanced PTE, which can be used to design other high performing NC photothermal agents.

References:

mechanisms of high-Tc superconductivity. These methods have further proven critical in understanding guest-host interactions, amorphous to crystalline transitions, local spin correlations, and other disordered crystalline materials phenomena. This lecture and tutorial is aimed at introducing neutron total scattering, community software, and refinement methods to new and beginning users. The lecture will focus in providing a technical foundation and highlighting exemplary work in the community, while the tutorial will include both demonstration and hands-on training with community software. We will also introduce available instruments (including our mail-in programs), sample environments, and resources for first time and beginning practitioners. A special emphasis will be placed on the growing number of in situ and in operando capabilities at the neutron total scattering beamlines at the Spallation Neutron Source at Oak Ridge National Laboratory.

1:30 PM
Synchrotron X-Ray and Neutron Diffraction Techniques for In-Situ and Operando Studies of Energy Materials Yang Ren; Argonne National Laboratory

This part of the tutorial will be focused on synchrotron X-ray and neutron diffraction techniques for in situ and operando studies of energy materials during synthesis and operation. General knowledge of synchrotron X-ray and neutron diffraction techniques and their complementarity for energy materials research will be introduced first. Some examples on synchrotron x-ray and neutron study of energy materials will be presented, e.g., in-situ/operando characterizing battery electrode materials during high temperature formation as well as during charging/discharging processes, in-situ probing transformation of ferroelectric ceramics under electric field or transforming alloys under mechanical stress, etc. Finally, future perspectives of synchrotron and neutron diffraction techniques for in-situ/operando study of energy materials will be discussed.

3:00 PM BREAK

3:30 PM
Local Symmetry Breaking in Functional Materials: A Tour from Quantum to Energy to Strange Emil Bozin; Brookhaven National Laboratory

The total-scattering-based PDF approach has been instrumental to understanding the local and intermediate range structure of complex functional materials. From standard to more advanced techniques, such as time resolved, dynamic, magnetic, thin film, and computed tomography approaches, the PDF method enables exploration of a diverse class of problems in contemporary material science. These include sustainable energy materials (e.g. battery and hydrogen storage materials, thermoelectrics), soft materials (e.g. drugs, polymers, sugars, cellulose), soft hard materials (e.g. strongly correlated electron systems, nanoparticles, catalysts), as well as materials displaying “strange” properties (e.g. negative thermal expansion, amorphization and amorphous materials, negative linear compressibility). This part will highlight the power of X-ray and neutron total scattering and PDF applications through selected illustrative examples. Focus will be placed on exploring dynamic local symmetry breaking in novel materials, emphasizing that this local symmetry breaking is the key for understanding devices from energy conversion to superconductivity. We will demonstrate that local, fluctuating broken symmetry states are widespread in functional materials.

SYMPOSIUM CP03

Advances in In Situ Techniques for Diagnostics and Synthetic Design of Energy Materials
April 23 - April 25, 2019

Symposium Organizers
Jenny Lockard, Rutgers, The State University of New Jersey
Chengjun Sun, Argonne National Laboratory
Feng Wang, Brookhaven National Laboratory
Markus Winterer, University of Duisburg-Essen

Symposium Support
Rutgers University - Newark Chancellor's Office
Rutgers University - Newark Department of Chemistry
The Advanced Photon Source (APS) at Argonne National Laboratory

* Invited Paper

SESSION CP03.01: Fast Transmission Electron Microscopy
Session Chair: Chengjun Sun
Tuesday Morning, April 23, 2019
PCC West, 100 Level, Room 101 C

10:30 AM *CP03.01.01
Development of a Dynamic Environment Transmission Electron Microscope for the Study of Ultrafast Light-Induced Phenomena in Nanoscale Materials Renske M. van der Veen1, 2; 1Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

In situ transmission electron microscopy has become a powerful technique to study functional nanomaterial dynamics in response to electrical, chemical, electrochemical, thermal, and/or electromagnetic fields prevalent under operating conditions. The time resolution, however, is typically limited by the maximum frame rate of the detector, which is at best in the kHz regime. Ultrafast transmission electron microscopy combines the high time resolution of laser spectroscopy with the excellent spatial resolution of electron microscopy techniques. The structural and electronic changes in the material are initiated by short (fs, ps, ns) laser pulses, which are followed by similarly short photoelectron pulses for probing the dynamics by means of imaging, diffraction, or energy-loss spectroscopy (EELS) within the electron microscope. In this talk I will present our dynamic environment transmission electron microscope (DETEM) at the University of Illinois. This versatile instrument enables time-resolved in situ studies of fast (fs-ms) material processes in gaseous and liquid environments that are triggered by light, heat, chemical flux, electrical bias or strain. I will give examples of studies using light excitation as the trigger, including nanosecond-resolved single-nanoparticle electron diffraction and real-space imaging of spin crossover phase transitions and ultrafast (fs, ns) EELS of light-induced dynamics in graphite thin films.

11:00 AM CP03.01.02
An Open Cell System for Probing Nanoparticles Under Illumination in Aqueous Solutions in an Environmental Transmission Electron Microscope Barnaby D. Levin1, Diane Haiber1, Qianlang Liu1, 2 and Peter Crozier1; 1Arizona State University, Tempe, Arizona, United States; 2Intel Corporation, Portland, Oregon, United States.

Nanoscale and atomic scale interactions between light and matter in water govern a number of important processes. One example is photocorrosion, which negatively impacts many areas including energy conversion technologies and structural materials. The process takes place in aqueous environments and, for semiconductors, is driven by electron-hole
pair generation from photon illumination[1-3]. For example, cadmium sulphide (CdS) based photocatalysts, undergo severe photocorrosion during photocatalytic water splitting[4]. Understanding the nano- and atomic scale changes induced by photocorrosion may offer new insights into fundamental questions regarding the initiation and evolution of photocorrosion and the impact of factors such as the presence of solute ions.

To probe photocorrosion and other light/matter interactions in solution, we have developed an open cell method for condensing liquid water around nanoparticles and illuminating them inside an environmental transmission electron microscope (ETEM). To facilitate liquid water formation, nanoparticles are dispersed on a TEM sample grid alongside ball milled sodium chloride (NaCl), which are strongly hydrophilic[4]. Samples are loaded into the ETEM in a cryogenic holder held at ~5°C, and are then exposed to 4–10 Torr of water vapor in the ETEM column, causing water droplets to form and dissolve the NaCl, and enveloping neighbouring nanoparticle clusters in NaCl solution. To illuminate particles immersed in solution, we have modified an earlier in situ light system[5] to use a 405 nm laser connected to the TEM with an optical fibre inserted through the objective aperture port of the microscope.

Aberration corrected TEM imaging before and after exposure to light and water will allow us to characterize changes that occur in clusters of particles. We apply this technique to CdS photocatalyst nanoparticles in a variety of light and solute conditions.

References:

We gratefully acknowledge support from the U.S. DOE (DE-SC0004954) and ASU’s John M. Cowley Center for High Resolution Electron Microscopy.

Composition Analysis by EDS at Elevated Temperatures in STEM and SEM Meiken Falke and Igor Nemeth; Bruker Nano GmbH, Berlin, Germany.

Energy dispersive X-ray spectroscopy (EDS) experiments at elevated temperatures up to the range of 1000°C, will be used to discuss challenges in in situ spectroscopy and element mapping. Heat radiation at elevated temperatures changes the low energy part of EDS spectra. Still, low energy element ID and chemical phase analysis are available in STEM and SEM within certain limits. The agglomeration and evaporation of material in a Pt-Au-nanoparticle test structure during heating in a conventional STEM were evaluated using statistical methods and phase analysis for. The results demonstrate the capabilities of in-situ EDS. The heating holder and its stability at changing temperatures plays a crucial role for successful experiments[1].

Further options of using EDS for in situ analysis are explored. One certain request is speed. Optimum photon detection geometry is crucial for efficient EDS in the electron microscope. Important to achieve that are a large solid and high take-off angle for photon collection, good collimation and suitable sample holders. The holders should not shadow the detector(s). Multi-detector arrangements enable large solid angles at high take-off angle particularly easily. Geometric optimization in combination with high brightness electron sources and aberration correction allows the identification and tracking of single atoms at low accelerating voltages in STEM within a few seconds[2]. Specimen holder materials and window materials need to be well known to ensure correct quantitative analysis of spectroscopic results, which is of particular interest in case of reaction cells holding liquid samples. Additionally, dealing with constantly changing data streams demands new ways of data acquisition and processing, which are being developed.


Composition Analysis by EDS at Elevated Temperatures in STEM and SEM

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In Situ Atomic-Scale Observation of Intermediate Pathways of Melting and Crystallization of Supported Bi-Nanoparticles in the TEM Leonard D. Francis; Department of Advanced Electron Microscopy, Imaging and Spectroscopy, International Iberian Nanotechnology Laboratory, Braga, Portugal.

Melting and crystallization are fundamental and practically important first-order phase transitions in condensed-matter physics, material science and climate change, yet a detailed understanding of their relevant kinetic pathways is still evolving[1,2]. To date, many theoretical models have been developed from homogeneous classical nucleation theory (CNT) model, but they rarely address the exact preferential nucleating sites and the potentially relevant role played by defects, surfaces, dimensionality and their combinations in phase transformations[3]. Recently, Samanta et al. conducted large-scale atomistic calculation of a phase transformation process of a metal from solid to liquid and predicted that the process takes place via multiple competing pathways involving the formation and migration of point defects or dislocations[4]. Although these calculations indeed provide a rare look at real phase transformations, much confusion still exists regarding the atomistic understanding of a dynamic process of a phase transformation due to the lack of direct experimental observations at the atomic scale as well as due to the experimental intricacies in tackling such a challenging topic. Bismuth (Bi) is an ideal inorganic model material suitable for gaining insights into nucleation dynamics due to its low melting point (even down to room temperature due to size effect).

Here, we report in-situ atomic-scale observations of a real dynamic process of melting or crystallization in supported Bi nanoparticles under heating or cooling conditions using a heating holder within an aberration-corrected (scanning) transmission electron microscope. We provide direct evidence that pre-nucleation in either melting or crystallization takes places via multiple intermediate state pathways involving the formation and migration of domain boundaries, dislocations and the ordering of interface and surface at the atomic scale. The pre-melting of the nanoparticle is a first at a grain boundary and expands to interfaces and dislocations and finally undergoes a catastrophic transformation from a solid-liquid state to a liquid droplet as a whole in a rather short time at high take-off exceeds a threshold value. When the size is smaller than the threshold value, the melting of nanocrystals takes place via two barrier-crossing pathways, i.e. pre-melting at grain boundary and a catastrophic solid-liquid transformation. Interestingly, pre-crystallization in a droplet occurs first at a solid-liquid interface and subsequently at the liquid surface, and eventually the droplet undergoes a fast complete transformation to a solid nanocrystal when undercooled. Thus the ability to conduct in-situ atomic-scale observation of the evolitional pathways in phase transformations of supported nanoparticles represents a significant step forward in understanding microscopic mechanisms of phase transitions at the atomic scale. The findings in the present study demonstrate that the melting/crystallization processes cannot be viewed as a simple single barrier-crossing event but as a complex multiple intermediate state phenomenon, which enhances our general understanding of nucleation and growth, melting/crystallization phenomena, phase transformations and helps to clarify atomic origins of temperature dependent behaviours in other nanomaterials and thin films[5].

References:

Effects of Pulsed Electron-Beam Characteristics on Radiation-Sensitive Materials for Energy Applications Elisah VandenBussche and David J. Flannigan; University of Minnesota, Minneapolis, Minnesota, United States.

In the understanding of durability and longevity of emerging photovoltaic materials, an essential component is the study of structural stability in response to photoexcitation. The study of photoinduced structural dynamics in inorganic semiconductors, such as silicon and gallium arsenide, has been established over recent years[1,2], thus enabling insights into thermal- and carrier-transport properties, especially pertaining to the effects of morphology and defects. Ultrafast electron microscopy (UEM), a pump-probe technique that utilizes a pulsed photoelectron beam generated by a femtosecond (fs) pulsed laser to extend the conventional capabilities of transmission electron microscopy (TEM) into the ultrafast (fs to picosecond) time domain[3], is one technique by which such studies can be conducted. Indeed, accessing the picosecond-nanometer spatiotemporal parameter space in the study of radiation-sensitive organic materials would doubtless allow for the discovery and the elucidation of light-induced excitation and decay mechanisms, especially with
Investigation of Aqueous Interfaces Using Ambient Pressure XPS

with experimental binding energies that have been determined from studies of copper based catalysts. Where there is ambiguity about experimental peak assignments, the

Using this method, we have calculated C1s nad O1s core electron binding energy shifts for a series of adsorbates on the Cu(111) surface. The results are in good overall agreement

delta-SCF method. We have carefully examined the convergence of the results with respect to the size of the cluster used to model the surface, and found that finite size effects can

optimized using a periodic slab model of the surface. Then, a cluster is cut from the slab, and the core electron binding energy is calculated for that cluster using the all-electron

calculation of core electron binding energies of surface species that combines the use of slab and cluster models of the surface. In the first step, the geometry of the adsorbate is

can be extremely challenging, for example when reference data that is typically used to guide "peak-assignment" is either unavailable or conflicting.

Recent developments in X-ray Photoelectron Spectroscopy have enabled studies, in which the surface chemistry of catalytically active materials is probed under quasi in situ

conditions. However, the insight into the mechanisms of catalytic reactions gained from such studies is entirely dependent on our ability to interpret the recorded spectra. Often this

Elevated pressure at which these experiments have to be carried out, but equally so the preparation of clean, well controlled aqueous samples with high cleanliness and

covered by a thin liquid-like layer (see Figure, which is adapted from Ref. [1]). The challenge for XPS experiments on aqueous interfaces under ambient conditions is not only the

surface of aqueous solutions in the presence of the equilibrium vapour pressure as well as trace gases, and the surface of ice, which at temperatures close to the melting point is

splitting of water, weathering of rocks, cloud droplet nucleation, the concentration of trace gases in polar regions, and thunderscloud electrification. [1,2] A detailed understanding of these processes requires the investigation of aqueous interfaces with chemical sensitivity and interface specificity under ambient conditions, i.e., temperatures above 200 K and water vapour pressures in the milliTorr to tens of Torr pressure range. Ambient pressure X-ray photoelectron spectroscopy [3,4] is an excellent method to probe the heterogeneous chemistry of these interfaces and has been applied to a number of different aqueous interfaces, including ultrathin water films on metals and oxides, bulk liquid/solid interfaces, the surface of aqueous solutions in the presence of the equilibrium vapour pressure as well as trace gases, and the surface of ice, which at temperatures close to the melting point is covered by a thin liquid-like layer (see Figure, which is adapted from Ref. [1]). The challenge for XPS experiments on aqueous interfaces under ambient conditions is not only the elevated pressure at which these experiments have to be carried out, but equally so the preparation of clean, well controlled aqueous samples with high cleanliness and reproducibility. In this talk we will review the progress that has been made in the area of APXPS experiments on aqueous systems and provide an outlook on opportunities for future research in this field.

1:30 PM *CP03.02.01
Investigation of Aqueous Interfaces Using Ambient Pressure XPS Hendrik Bluhm1, 2; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Fritz Haber Institute of the MPG, Berlin, Germany.

Aqueous interfaces are ubiquitous in technological applications and in the environment and govern numerous important phenomena, including corrosion, photoelectrochemical splitting of water, weathering of rocks, cloud droplet nucleation, the concentration of trace gases in polar regions, and thunderscloud electrification. [1,2] A detailed understanding of these processes requires the investigation of aqueous interfaces with chemical sensitivity and interface specificity under ambient conditions, i.e., temperatures above 200 K and water vapour pressures in the milliTorr to tens of Torr pressure range. Ambient pressure X-ray photoelectron spectroscopy [3,4] is an excellent method to probe the heterogeneous chemistry of these interfaces and has been applied to a number of different aqueous interfaces, including ultrathin water films on metals and oxides, bulk liquid/solid interfaces, the surface of aqueous solutions in the presence of the equilibrium vapour pressure as well as trace gases, and the surface of ice, which at temperatures close to the melting point is covered by a thin liquid-like layer (see Figure, which is adapted from Ref. [1]). The challenge for XPS experiments on aqueous interfaces under ambient conditions is not only the elevated pressure at which these experiments have to be carried out, but equally so the preparation of clean, well controlled aqueous samples with high cleanliness and reproducibility. In this talk we will review the progress that has been made in the area of APXPS experiments on aqueous systems and provide an outlook on opportunities for future research in this field.


2:00 PM CP03.02.02
Observing Reactions at Surfaces with Fast and Dynamic XPS Christian Kaiser, Burkhard Krömker and Georg Prümper; Sigma Surface Science GmbH, Taunusstein, Germany.

Fast XPS is a popular method for observing reactions and transitions at surfaces. The combination of chemical analysis and surface sensitivity with fast and time resolved data acquisition offers insight into the process itself where “static” measurements merely show its outcome.

Applications can be found in many fields of research where the nature of the process is studied, e.g. on-surface synthesis of polymers and 2d materials, adsorption mechanisms during solid-gas interactions or thermally activated reactions at surfaces.

This method is mostly applied at synchrotron beamlines where short acquisition times for time resolution are compensated by high photon flux for signal strength. In this talk enhancement of this measurement technique due to recent advances in instrumental development is presented and demonstrated with applications. Not only does it increase the spectroscopic information to multiple, wide range peak areas, but opens up the possibility for off-line and laboratory based experiments with conventional X-ray sources on time scales down to the millisecond range. This way, parameters for controlled and reproducible processes or interactions can be found and optimised, and the dynamics of these processes systematically observed. Furthermore, specific properties important e.g. in device fabrication can be engineered with fast and dynamic XPS using its time resolved aspect.

2:15 PM CP03.02.03
The Role of First Principles Calculations in Interpreting Core Level X-Ray Photoelectron Spectra of Complex Heterogeneous Systems Juhan Matthias Kahk1 and Johannes C. Lischner2, 1Department of Materials, Imperial College London, London, United Kingdom; 2Department of Physics and Department of Materials, Imperial College London, London, United Kingdom.

Recent developments in X-ray Photoelectron Spectroscopy have enabled studies, in which the surface chemistry of catalytically active materials is probed under quasi in situ conditions. However, the insight into the mechanisms of catalytic reactions gained from such studies is entirely dependent on our ability to interpret the recorded spectra. Often this can be extremely challenging, for example when reference data that is typically used to guide "peak-assignment" is either unavailable or conflicting.

First principles calculations of core electron binding energies can guide the interpretation of experimental results. We have developed a computational framework for the calculation of core electron binding energies of surface species that combines the use of slab and cluster models of the surface. In the first step, the geometry of the adsorbate is optimized using a periodic slab model of the surface. Then, a cluster is cut from the slab, and the core electron binding energy is calculated for that cluster using the all-electron delta-SCF method. We have carefully examined the convergence of the results with respect to the size of the cluster used to model the surface, and found that finite size effects can be effectively reduced to the point where they are smaller than the functional error. Using this method, we have calculated C1s nad O1s core electron binding energy shifts for a series of adsorbates on the Cu(111) surface. The results are in good overall agreement with experimental binding energies that have been determined from studies of copper based catalysts. Where there is ambiguity about experimental peak assignments, the
In Situ shapes with \{hk0\} facets. Nonequilibrium shapes such as the THH are difficult to synthesize, so understanding the mechanisms of nonequilibrium etching could lead to

Previous work has shown that nonequilibrium etching of cubes with \{100\} facets and rhombic dodecahedra (RDD) with \{110\} facets leads to intermediate tetrahexahedra (THH)

relative amount of the oxidative species in solution which controls the oxidative potential of the etching environment. With this control of the liquid cell pockets, oxidative etching

trajectories. This technique shows where the ligands are binding on the nanocrystal as well as potential pathways to unique nanocrystal shapes.

nonequilibrium etching gives important directions for synthetic control of high index facets. The difference in coordination of newly exposed atoms causes the differing chemical potential dependence. This mechanistic insight into

beam dose rate controls the amount of oxidative species in solution, and the etching rate varies linearly with the electron beam dose rate. The FeCl


3:30 PM  *CP03.02.04  
Electron Energy-Loss Spectroscopy for Designing Plasmonic Catalysts  Renu Sharma1,2, Wei-Chang D. Yang1,2, Alina Bruma1,2 and Canhui Wang1,2. 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2University of Maryland, College Park, Maryland, United States.

The energy barrier for most of the chemical reactions is overcome by heating the reactants in the presence of a suitable catalyst, where the thermal energy provided by heat helps in surpassing the barrier that has been reduced by the adsorption of the reactant molecules on the catalyst nanoparticle surfaces. In recent years, localized surface plasmon (LSP) resonance energy has been used to replace the thermal energy to initiate reaction at low temperatures, even at room temperature.1,2 As most of the plasmonic materials, Au, Ag or Al, are not generally catalytically active, they have been successfully used by combining them with active catalysts such as Pt, Ni, Ru, etc. Most of the researchers so far have used optical methods to generate and measure the LSP resonance energies. However, the combination of low spatial resolution, of the order of 100 nm, achievable by optical methods, does not provide sub-particle level distribution of coupling efficiency of different modes. On the other hand, high energy electrons not only excite all LSP modes simultaneously, but also provide high spatial resolution in the nanometer range to resolve their energy loss probability that indicates the efficiency of coupling the location-specific electron excitation of the LSP modes at certain resonance energies on the plasmonic nanoparticle. Therefore, we use a monochromated electron source in an environmental scanning-transmission electron microscope (ESTEM), combined with metallic nanoparticle boundary element method (MNPBEM) and density functional theory (DFT) simulations, to characterize various LSP modes and their coupling efficiency distribution within the shape and size-controlled nanoparticles of Au and Al. We demonstrate that the knowledge gained from low-loss and core-loss EELS measurements can be used to design catalyst-plasmonic particle combination for selected chemical reactions.


3:00 PM BREAK
This work provides mechanistic insight into the shape transformations of nanocrystals in their native liquid environment. In addition, the development of chemical control in the liquid cell will open up future opportunities for materials researchers who seek to further understand a variety of nanoscale systems.

4:15 PM CP03.03.03
In Situ Diagnostics of 2D Materials Synthesis and Heterogeneity—Closing the Loop for Functional Optoelectronic Materials
David B. Grohogan1, Yu-Chuan Lin1, Yilang Yu1, Chenze Liu1, Gerd Duscher2, Alex Strasser1,3, Alexander Puretzky1, Kai Wang1, Minu Yoon1, Christopher M. Rouleau1, Stella Canulescu1, Philip D. Rack1, Liangbo Liang1, Gyula Eres1 and Kai Xiao1;
1Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, United States; 3Texas A&M University, College Station, Texas, United States; 1DTU Fotonik, Technical University of Denmark, Lyngby, Denmark.

Atomically-thin two-dimensional (2D) layered materials, especially the semiconducting 2D transition metal dichalcogenides (TMDs) and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, and quantum information science. However, significant synthesis and processing challenges currently limit their development, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. While this heterogeneity offers a serious challenge for synthesis and processing, it also offers a tremendous opportunity to tailor functionality. In situ spectroscopic diagnostics during the synthesis and processing of 2D materials offers a rare chance to ‘close the loop’ between synthesis and properties to tailor optoelectronic functionality with real-time feedback.

Here we present principally non-equilibrium, laser-based synthesis and processing approaches for the synthesis and processing of 2D TMD materials that permit correlated in situ spectroscopy and imaging measurements as real-time diagnostics of heterogeneity. First, advances in pulsed laser deposition (PLD) of 2D TMDs (e.g., MoS2, WSe2) at elevated temperatures are described using in situ diagnostics of the growth environment (e.g., ICCD imaging and ion probe characterization of the plasma plume) and in situ diagnostics of the growing film (e.g., in situ laser reflectivity) to understand and optimize the growth process. Structure, composition, and heterogeneity of the films are characterized principally with AFM, atomic resolution HA-ADF STEM microscopy, and EELS.

Through this understanding and tuning of the PLD process, energetic atoms/molecules, to clusters and amorphous nanoparticles can be utilized for synthesis. Two effects will be presented. First, the effect of high kinetic energy atomic and molecular species to directly convert existing 2D crystals into alloys by chalcogen replacement is explored using photoluminescence and Raman spectroscopy as diagnostics of band gap shift and structure. Selective conversion of bilayer crystals is possible with this technique to form vertical heterojunctions. Second, amorphous nanoparticle ‘building block’ precursors are deposited as precursors for subsequent laser annealing studies to understand the timescales and mechanisms for their crystallization and evolution into 2D layers. This conversion is studied at two levels. First, in a custom vacuum microchamber under an optical microscope tailored for in situ Raman spectroscopy, absorption spectroscopy, photoluminescence, and SHG mapping. And second, in a prototype setup that allows laser illumination to be coupled into a (scanning) transmission electron microscope (TEM) for real-time observations of nonequilibrium synthesis directly on TEM grids.

These laser-based synthesis and processing approaches, coupled with in situ spectroscopic and imaging diagnostics, allow the stepwise evolution of synthesis to structure and optoelectronic function to be correlated through association theory and modeling, forming a novel strategy to ‘close the loop’ for directed synthesis.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science). Throughout the presentation, facilities available for collaboration at the Center for Nanophase Materials Sciences (CNMS) user facility will be presented.

4:30 PM *CP03.03.04
About Using In Situ and Operando Characterization to Characterize Catalysts
Jeroen A. van Bokhoven; ETH Zurich-PSI, Zurich, Switzerland.

The complexity of the catalytic process makes it difficult to capture the structure of the catalytically active sites. The catalytic process occurs at multiple time- and length-scales and the structure of a heterogeneous catalyst is non-uniform and deciding which of the observed species is relevant for catalysis is far from obvious. Simplification of the system by using model structures and conditions helps to determine structure – performance relationships. However, such model systems and conditions are not necessarily relevant to the actual catalytic process. Determining the structure of a catalyst while it performs its catalytic function is the domain of operando characterization and is seemingly the best way of capturing structure – performance relations. Performing an operando characterization does not necessarily yield the catalytically relevant structures. Catalysis occurs over reactive surfaces, which may change their structure upon interaction with reactants, intermediates and products. During catalytic conversion reactants are converted into intermediates and products, thus changing the gas composition. With such change, the catalyst surface and its catalytic reactivity may change in accord. Thus, multiple structures as function of position within the reactor may exist. Also, the observation of structure in an operando experiment is no guarantee that that structure is relevant to the catalytic reaction. When taking into account relatively simple concepts from reaction kinetics, a distinction between spectator and active species can be made.

SESSION CP03.04: Poster Session: Advances in In Situ Techniques for Diagnostics and Synthetic Design of Energy Materials
Session Chairs: Jenny Lockard, Chengjun Sun, Markus Winterer and Markus Winterer
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

CP03.04.01
Light-Driven Liquid Cell Transmission Electron Microscopy to Study Photocatalytic Materials

Recent advances in liquid cell transmission electron microscopy (TEM) have enabled the study of reactions in liquid-solid interface at high spatial resolution in real-time environment. The capability to apply stimuli such as electrical, heating and electrochemical measurements has already started to provide new insights on the dynamics and structural changes during nanoparticles synthesis1, lithium charge and discharge2, crystal growth3 and metal corrosion4. The further ability to introduce light within the confined liquid environment of TEM strengthens the capability by allowing the study of light interaction in materials during reaction at solid-liquid interface, thus enabling photoelectrochemistry in TEM. The study of hydrogen generation via photoelectrochemical method5 is one relevant application that can benefit from this technique and can provide fuel for energy storage solution in a clean and environmentally friendly way. However, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting for efficient hydrogen generation are currently poorly understood. Further understanding of the role of various photocatalysts and the physics governing the active hydrogen evolution sites will allow for better and efficient design of photovoltaic devices. Here we present the development of a unique in-situ liquid TEM holder with photo-capable light source to study photocatalytic reactions in real time at nanometer length scales. Using some of the model materials such as Au nanoparticles and MoS2 flakes, we will present the correlation of I-V characteristics with water splitting and simultaneous structural changes at the catalytically active sites. For accurate quantitative information and reliability of materials interface in liquid, we will also present strategies to deposit materials of interest in the desired electrodes of liquid cell chips by using an inkjet materials printer. The availability and utilization of photo stimuli in liquid cell TEM can provide important fundamental insights into the understanding of several other photoelectrochemical systems.

References:
Two-dimensional (2D) materials have been extensively studied in recent years due to their unique properties and great potential in energy-related applications, such as hydrogen evolution reaction (HER) and CO₂ reduction reaction (CO₂RR). To gain in-depth atomic-level understanding on the correlation between the catalytic surface and reaction mechanism, we employed ambient pressure X-ray photoelectron spectroscopy (APXPS) to investigate the electronic and chemical properties of Mo₅S₃ interfaces at various environments. Our APXPS data showed a pristine Mo₅S₃ ultrathin film surface exposed to CO₂/H₂O ambient formed several intermediates, including physisorbed (linear form, f-CO₂) or chemisorbed (bent form, b-CO₂) CO₂ states and oxygenate species, such as hydroxyl, formate or carbonate groups. The adsorption configuration of CO₂ (f-CO₂ vs. b-CO₂) depends on the experimental conditions. If we introduced CO₂ then H₂O, more physisorbed CO₂ were detected; in contrast, if H₂O were introduced first then CO₂, more chemisorbed CO₂ were obtained. Identifying the first CO₂ adsorption step is to promote initiation of reaction steps. Furthermore, the valence band offset was also observed due to surface band bending during CO₂ reduction reaction. While CO₂ can induce upward surface band bending due to an acceptor molecule CO₂ has accepted electron from Mo₅S₃ semiconductor surface, co-dosing H₂O into system facilitates the adsorbing molecules to take holes from Mo₅S₃ semiconductor surface, consequently, induces downward band bending on semiconductor surface.

Our APXPS results suggest a strong correlation between the electronic and chemical properties of the material surface during catalytic reaction. The results in this study have added our understanding of the underlying mechanism involved in catalytic reaction, and helped us gain insights in designing and improving CO₂ reduction catalysts.

CP03.04.05
In Situ Analysis and Simulation of Heat Generation During Charging and Discharging of Ni-Rich Layered Oxide Cathode Gaheee Kim, SAI, Suwon, Korea (the Republic of).

Thermal management and design are very important for lithium-ion batteries (LIBs) to prevent thermal runaway under normal and abnormal conditions such as overcharge and short circuit. In this study, in-situ thermal analysis was performed on LiNiO₂-rich cathode materials. We have investigated the layer structure of a powder sample to determine the phase composition of the material. The thermal behavior of the sample was recorded during the charging and discharging cycles. The results show that the charging and discharging processes are accompanied by changes in the temperature profile of the material. The thermal performance of the battery was also analyzed and compared with the theoretical predictions. The simulation results were in good agreement with the experimental data, indicating the reliability of the simulation approach.

CP03.04.06
Rapid High Shear Viscosity Measurements Using a Microfluidic Rheometer Matt Vandcn Eynden 1, Thanina Amiar 1, Hubert Ranchon 2 and Gerard Meunier 2; 1Formulation, Inc., Worthington, Ohio, United States; 2Formulaclon, Toulouse, France.

Viscosity is an essential physical property when studying the rheological behavior. However, rheological studies remain a challenging task for many laboratories, as traditional techniques are time-consuming and face to volatility and drying issues. In a new approach to confined, high shear viscosity measurements, a novel microfluidic rheometer is equipped with an enclosed system suitable for volatile and fast drying products, providing viscosity measurements as a function of shear rate and temperature in a single experiment set-up with an excellent precision and accuracy even at very low viscosity values. Visual analysis of a laminar flow interface generated from a reference and an unknown sample allows for viscosity to be measured by taking a picture of the main channel inside the microfluidic chip, using dedicated algorithms to automatically extract viscosity data over a controlled range of shear rates and temperatures. The technology allows flow viscosity measurements of liquid products from water-like to thick formulations using a small amount of product under a wide range of shear rates from 10³ to 10⁶ s⁻¹. In the work, we have analyzed a model blend of two solvents aimed for Li-ion electrolyte batteries at 35 °C consisting of dimethyl carbonate, ethyl methyl carbonate and dissolved lithium salts.

CP03.04.07
Dopant Profiling Using Low-Voltage SEM for GaN Power Electronics Shantan Reddy Alagubeli 1, Houqiang Fu 2, Kai Fu 2, Hansxiao Liu 1, Yujie Zhao 2 and Fernando A. Ponce 2; 1Department of Physics, Arizona State University, Tempe, Arizona, United States; 2School of Electrical, Computer and Energy Engineering, Arizona State University,
GaN is a material of interest for power electronics due to its high critical breakdown electric field of 3.3-3.75 MV/cm, compared to 0.3 MV/cm for silicon. A typical GaN-on-GaN power device has regions that are doped differently. For example, vertical- junction field-effect transistors (VJFTs) have p-GaN regions as the gate, intrinsic regions as the drift layer, and the n-GaN region as the source and drain. Identifying these regions with a good spatial resolution is critical for the understanding of the device characteristics and failure analysis after malfunction. Dopant sensitive techniques like SIMS, electron holography are destructive and time consuming. Also, SIMS does not have the capability to resolve lateral variations in the layer design.

Low-voltage scanning electron microscopy has been used to study dopant contrast in GaN p-i-n epitaxial structures for power electronics applications. Secondary electron emission intensity is highest from p-layer and lowest from the unintentionally-doped (UID)-layer. Quantification of dopant contrast requires identification of all the parameters effecting the secondary electron emission intensity. In this work, we discuss about the factors effecting the secondary electron emission intensities from p-, i-, and n-type GaN layers. Also, we examine the effect of surface preparation on the dopant contrast. This technique is reliable for dopant profiling in GaN power electronics.

CP03.04.08
Non-Uniform Mg Doping in GaN Epilayers on Mesa Structures
Hanxiao Liu, Houqiang Fu, Kai Fu, Shanthan Reddy Alugubelli, Yuji Zhao and Fernando A. Ponce
Department of Physics, Arizona State University, Tempe, Arizona, United States; School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States.

Gallium nitride (GaN) based power electronics has attracted much attention in recent years due to its advantages over traditional Si-based power devices in terms of energy conversion efficiency, switching speed, operation temperature, and system size. In the fabrication of advanced vertical power devices, such as junction barrier Schottky diodes, superjunction diodes, and normally-off vertical junction field effect transistors (VJFTs), it is important to produce laterally patterned p-n junctions, i.e., alternating n-type and p-type regions arranged in lateral directions. However, the mechanism of selective area doing of GaN is poorly understood. The characterization of the lateral dopant distribution in selectively doped GaN regions is difficult, due to the spatial resolution limitation of secondary ion mass spectroscopy. In this work, selective area p-type doping of GaN on GaN bulk substrates was achieved by etching and epitaxial regrowth. The optical properties of p-GaN epilayers grown on an unintentionally-doped GaN mesa structure have been studied using spot mode cathodoluminescence (CL) and monochromatic CL mapping. A strong variation in the luminescence characteristics has been observed, with the sidewall of the mesa structure being different to the flat upper and lower mesa regions. A comparison with luminescence characteristics of p-GaN films grown with different Mg concentrations indicate that the Mg concentration at the sidewall is significantly lower. The lower Mg concentration at sidewall is attributed to inefficient Mg incorporation of semi-polar growth. This work demonstrates that CL spectroscopy can be used as a nondestructive, contact-free method to probe local p-GaN doping distribution with submicron resolution. The determination of Mg distribution in p-GaN on a mesa structure is important for GaN-based power devices.

CP03.04.09
Identification of Point Defects in BAIN Using High-Resolution Electron Energy Loss Spectroscopy
Shuo Wang, Katia Mareh, Peter Rez and Fernando A. Ponce; Arizona State University, Tempe, Arizona, United States.

Although there are many techniques that can detect bandgap GaN regions associated with point defects in the lattice, it is not routinely possible to determine the type of defect at submicron spatial resolution. Here we show that high-resolution electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope can locate and identify point defects with a sub-nanometer probe in a wide-bandgap BAIN semiconductor.

Two BAIN thin films of 50 nm thickness were grown by metalorganic chemical vapor deposition on top of AlN templates, with B/(B+Al) gas-flow ratios of 0.12 and 0.18, respectively. In the atomic-resolved high-angle annular dark-field images, the two films exhibit considerable variation in the B concentration. The high-resolution monochromated spectra from the high B concentration BAIN film taken at 60kV show energy losses in the bandgap region. The film with low B concentration has similar energy thresholds, but with lower intensities. These energy-loss thresholds are still detectable in the AlN substrate, although with diminishing intensity as the beam is moved further from the interface, due to the long-range nature of the electromagnetic interaction. Since there is an analytical theory for the spatial variation of the signal as a function of distance between the probe and the dipole, it would be in principle possible to fit this functional form to the observed signal to localize the dipole with nanometer resolution.

To identify the origin of these features, calculations of densities of states with the VASP Density Functional Theory (DFT) code were used to explore whether postulated point defects give rise to states in the band gap, and whether transitions involving these states match experimental observations. VASP DFT calculations were performed using projection augmented wave, local-density approximation potentials for single Al, B and N interstitial atoms, single Al and N vacancies in a supercell constructed from 3x3x2 AlN unit cells. Although the bandgap energy is underestimated as 4.6 eV, it could be argued that the DFT energies for the point defect states are reliable. In our calculations, there are no bandgap states when B is substituted for Al, and the density of states is very similar to that of AlN. In all the other cases the calculations showed states in the band gap, consistent with previous reports on point defects in AlN. The EELS thresholds at 0.39 eV and 0.79 eV respectively, are attributed to B interstitials. It is expected that they would be present in both the high and low concentration B films, albeit with lower intensity in the lower concentration film, given that the solubility limit of B in AlN is reportedly 2.8%. It would seem that other thresholds at 0.53 eV and 0.66 eV, arise from N or Al vacancies, and possibly Al interstitials. Not surprisingly these thresholds attributed to displaced Al and N atoms are more likely in the film with higher B concentration.

CP03.04.11
In Situ Electron Beam Induced Current STEM Measurements of the Minority Carrier Diffusion Length in n-GaN
Zhao Wareck, Andrew Armstrong, Alec Talin and John Cunning; University of Maryland, College Park, Maryland, United States; Sandia National Laboratories, Livermore, California, United States.

Gallium nitride (GaN) offers several advantages over current silicon based devices, such as temperature applications, high-power electronics, and space-based or other high radiation exposure applications [1]. Measurements of the minority carrier diffusion length in GaN can be studied using cathodoluminescence (CL) or electron beam induced current (EBIC) in a scanning electron microscope (SEM). However, as recently reported in Yakimov et al., the EBIC planar geometry in SEM often leads to an over estimation of the minority carrier diffusion length in n-GaN [2]. This over estimation is attributed to the interaction volume in SEM, which is on the order of hundreds of nanometers to a few microns and within the same order of magnitude as reported minority carrier diffusion lengths of n-GaAs, which are reported to be between a few tens of nanometers to a few microns. Instead of SEM EBIC, we use bulk scanning transmission electron microscopy (STEM) EBIC to measure the minority carrier diffusion length in n-GaN. Our sample consists of a high purity single crystal n-type GaN substrate (275 µm thick) grown by hydride vapor phase epitaxy (HVPE) with a threading dislocation density of ~10^6/cm² and patterned with a nickle Schottky contact as well as an indium ohmic contact. Using a 100 kV or 200 kV accelerating voltage causes the interaction volume in our bulk specimen to be large enough to separate from the minority carrier diffusion length. We then fit the STEM EBIC line profiles in order to determine the minority carrier diffusion length of n-GaN as well as the interaction volume. In addition, we have imaged the growth of the depletion edge during an applied reverse bias, and indirectly measure the depletion width at zero applied bias.

This research was performed at the University of Maryland NanoCenter Advanced Imaging and Microscopy Laboratory. The data was taken on a JEOL 2100F TEM operating at 100kV and 200 kV in STEM mode using a NanoFactory STM-TEM holder.


The authors acknowledge funding from Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, the National Science Foundation Graduate Research Fellowship Program under Grant No. DGE 1322106, and support from NIST Grant No. 70NANB15H218. Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC0494AL85000.

CP03.04.13
In Situ TEM Biasing Experiments with Easy-to-Move Mobile Probes
Transmission electron microscopy (TEM) sample holders with biasing capabilities in which a mechanical mobile probe acts like one of the electrodes allow to investigate, simultaneously, the electrical properties of materials and their structural and chemical states, by using the full battery of characterization techniques available in a TEM (high-resolution imaging, electron-based spectroscopy, electron diffraction, etc.). This in-situ biasing microscopy technique has been used to investigate the conductance through rows of metal and carbon atoms [1,2], the switching of resistive memories [3], anode materials for batteries [4,5], etc. Here, we present several examples in where a recently developed in-situ TEM sample holder with a mobile probe was used to bias samples locally and discuss the practical considerations of the technique, with the objective of facilitating the experiments—which can be challenging during the mobile probe mechanical approach to the sample.

Specifically, we discuss how to approach the sample with coarse and piezoelectrically-driven fine movements and how to prepare the mobile probe, inside the TEM column, to obtain a good electrical contact between the sample and the probe prior to the experiment; by “good” we understand contacts without contamination or oxide layers that can disrupt the contact’s intrinsic electronic properties. The sample holder used during these experiments allows to approach the sample with the mobile probe in manual coarse mode with smooth and uncoupled steps of μm (or fractions of μm) among the three spatial axes. Likewise, it allows to do the final contact approach with a piezoelectric controlled mechanism that allows uncoupled nanometer-sized (or less) steps among the three spatial axes. We will present three examples: 1) observation of the Li-alloying process in yolk-shell p-Si nanorods/voids/nitrogen-doped carbon nanostructures relevant for anode materials in Li-ion batteries [4]; 2) the investigation of the high capacity retention of Sr2Te3/C composites relevant for sodium-ion batteries [5]; and 3) the reaction of a solid-sate electrolyte particles under load. These examples illustrate the convenience of this in-situ biasing technique when creating a contact prior to the experiment is difficult.

References:

CP03.04.14
Exploring the Interfacial Structure in Aqueous Colloidal Tin Dioxide Dispersions
Viktor Mackert, Thomas Winter and Markus Winterer; Nanoparticle Process Technology, Universität Duisburg-Essen, Duisburg, Germany.

Nanoparticles immersed in liquids (i.e. water or electrolyte solutions) change their solid-gas interface into a solid-liquid interface which substantially modifies the surface chemistry of the particles. Consequently, existing surface charges lead to an electrochemical double layer formation around the dispersed nanoparticles. Furthermore, the structure of the electrochemical double layer has a profound influence on reaction kinetics [1]. Many properties and applications of nanoparticles such as ion exchange, adsorption or catalytic reactions rely on the structure of the solid-liquid interface. The solid-liquid interface plays a major role in photocatalytic water splitting, electrocatalysis, solid-electrolyte batteries and fuel cells. SnO2 is a material that finds application as photocatalyst or in lithium ion batteries as anode material. Here, chemical vapor synthesized (CVS) SnO2 nanocrystals are studied with X-ray absorption spectroscopy (XAS) in liquid colloids. The local structural environment of tin dioxide – water interface is analyzed over a range pH values (using HBr and RbOH) and the ionic strength (RbBr) to reveal changes in the interfacial region due to the modified particle-ion interaction at the particle surface. XAS spectra at the Sn K-edge, Br K-edge and Rb K-edge are measured and compared to dry SnO2 nanocrystals.

Acknowledgement:

CP03.04.15
Designing Perovskite Nanoparticles to Probe Structural Changes During Catalytic Activity by In Situ X-Ray Absorption Spectroscopy
Jeremias Geiss and Markus Winterer; Faculty of Engineering, University of Duisburg-Essen, Duisburg, Germany.

Heterogeneous catalysis of photocatalytically active perovskite nanoparticles like LaFeO3 occurs by the interaction of molecules with active sites of the particle surface. While the crystalline core is resolved using conventional X-ray diffraction (XRD), structural changes of the boundary layer during catalytic activity are accessible by In situ X-ray spectroscopy (XAS) [1]. Since nanoparticles have a high ratio of surface to volume atoms, a large fraction of the measured signal originates from the surface. By Reverse Monte Carlo (RMC) analysis, pair distribution functions can be retrieved from XAS measurements which contain the structural evolution and information of the local structure of the particle and its surface.

To constrain the RMC model, it is important that the initial single particle model closely represents measured particles. Since in situ XAS is an ensemble measurement over thousands of individual nanoparticles, the measured nanoparticles must be phase pure, monodisperse, very small, highly crystalline and dispersible. The requirements of colloidal perovskite photocatalytic nanoparticles for in situ probing of the structure-activity-relationships are discussed and first ex situ measurements using RMC analysis will be presented.

References:

Acknowledgements:
This work is supported by the German Research Foundation (DFG) through the Collaborative Research Center 247, Projekt B01. The authors gratefully acknowledge the provision of XAS beamtime at Diamond and the Advanced Photon Source and support by Fred Moseleman and Sungik Lee at beamlines I20 and 12-BM-B.

CP03.04.16
Coupling Operando Electrochemical Mass Spectrometry with Post-Mortem Analysis of Electrodes for Revealing the Degradation Mechanisms of Electrochemical Capacitors During High Voltage Operation
Patryk Przygocki, Paula Ratajczak and Francois Beaugnon; Poznan University of Technology, Poznan, Poland.

Recently, the research on carbon/carbon electrochemical capacitors (ECs) is essentially dedicated to increase their extractable energy which is directly related to the maximum operating voltage of the electrode/electrolyte system [1,2]. Long-time operation at maximum voltage (so-called potentiostatic floating) accelerates ECs ageing, revealed by loss of capacitance, increase of resistance and internal pressure. The worsening of these three parameters is related to carbon surface oxidation and/or pore blockage by electrolyte decomposition products, together with ionic starvation in the electrode due to decrease of electrolyte concentration and gas evolution which entails weakening of the adhesion between the active mass and the current collectors [3,4]. Besides, the surface of the aged positive carbon electrode is modified by new oxygenated groups, while the aged negative electrode is also functionalized, although one could expect that it should not occur at this electrode under reductive conditions. Indeed, H2O2 which is first produced at the positive electrode as by-product of water electrolysis, migrates through the separator towards the negative compartment being then further involved in oxidation of the carbon surface [5].

In this context, it will be shown that it is possible to obtain information about all the realistic mechanisms of ECs ageing as well as to determine the relative impact of each process on the system degradation by using a combination of operando analyses consisting of electrochemical measurements, mass spectrometry and cell pressure records, together with post-mortem surface functionality analysis of individual carbon electrodes by temperature programmed desorption (TPD). On the example of an electrochemical carbon/carbon capacitor in aqueous Li2SO4, the approach is based on assigning the charge passing through the cell under potentiostatic floating (known as leakage current) to the charge: i) spent at each electrode for production of gases (taking into account operando EMS analysis and pressure records); ii) utilized to oxidize the electrodes surface (from post-mortem surface functionality analyses realized by TPD); iii) being redistributed throughout the electrochemical cell (taking into account the steady-state leakage current measurements).
Colossal Transformations in Metal-Organic Frameworks with Ultrahigh Porosity

Stefan Kaskel1,2, Fraunhofer IWS, Dresden, Germany; Chemistry, TU Dresden, Dresden, Germany.

Metal-Organic Frameworks (MOFs) have become promising alternatives for gas storage and sensing applications. However, the ultrahigh porosity of MOFs often results in low structural stability due to the presence of defects and vacancies. In this work, we introduce a novel strategy to fabricate ultrahigh porous MOFs with improved stability by employing a combination of high-temperature synthesis and post-treatment techniques.

Abstract: The synthesis of ultrahigh porous MOFs involves a balance between structural stability and accessibility for gas adsorption. By optimizing the synthesis conditions and applying post-treatment methods, we have achieved the highest reported porosity in MOFs, exceeding 23.4 mA/cm² for CO₂ capture via In Situ DRIFTS Techniques. The characterization of these materials using advanced techniques such as Time-Resolved Thermoreflectance and X-ray Powder Diffraction has revealed unique structural and mechanistic insights into the CO₂ capture process.

Keywords: Metal-Organic Frameworks, Ultrahigh Porosity, CO₂ Capture, In Situ DRIFTS, Time-Resolved Thermoreflectance.

In Situ Measurements of Plasma-Surface Interactions via Time Domain Thermoreflectance—Electron Heating, Surface Cooling and Chemical Reactions in Materials

Patrick Hopkins1, John A. Tomko1 and Scott Walton1; 1University of Virginia, Charlottesville, Virginia, United States; 2U.S. Naval Research Laboratory, Washington, DC, District of Columbia, United States.

The energy flux to a surface during plasma exposure and the associated surface heating are of long standing interest as they contribute to the physico-chemical changes that occur during plasma-based materials synthesis and processing. Indeed, the energy delivered to the surface, via a flux of particles and photons, in concert with a flux of reactive species serves to chemically modify, etch, and/or deposit materials, with an efficacy that depends on the plasma processing environment. A unique feature of plasma synthesis and processing is that most of the delivered energy is absorbed at or very near the surface over short (picosecond) time scales. The dissipation of thermal energy proceeds through electron-electron and/or electron-phonon interactions as they propagate through the material, with relaxation time scales that can be orders of magnitude slower. Typically then, the surface is not in thermal equilibrium with the bulk material. Fast, surface-sensitive techniques are thus required to fully appreciate the dynamics of the plasma-surface interaction.

In this work, we employ pump-probe Time-Domain Thermoreflectance, a surface sensitive technique typically used to measure thermal properties of thin films, to determine electron heating of thin metal films during exposure to an atmospheric pressure plasma jet. The results, in conjunction with current measurements, are used to develop a first order understanding of plasma jet-surface interactions. The results show that the energy delivered by the plasma jet causes a localized increase in electron energy within the thin film over an area commensurate with the plasma jet radius. We also describe measurements in which we monitor the temperature evolution of the surface during plasma exposure and plasma excitation, demonstrating both heating and cooling due to chemical changes to the surface.


Jonathan Holmér1,2,3,4, Lubjana Zeng1,2,3,4, Thomas Nordkvist2, Peter Kroegstrup2, Jesper Nygård2, Ludvig de Knop1 and Eva Olsson1; 1Chalmers University of Technology, Gothenburg, Sweden; 2Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark.

Semiconductor nanowires are promising building-blocks for the next generation of solar cells. With diameters of a few hundred nanometers, vertical nanowires can act as waveguides for the incoming sunlight and thereby enhance the light absorption. The nanowire geometries further enable the growth of defect-free heterostructure interfaces including also defect-free growth on lattice mismatched substrates, not possible for bulk structures due to the magnitude of interfacial strain. Because of these and other unique properties, nanowire-based solar cells have the potential to provide higher efficiencies and lower material costs than their thin-film counterparts. One of the main challenges for realizing these high-performance nanowire solar cells lies in the optimization of the electrical and photocatalytic properties at the individual nanowire level. Here characterization techniques play a vital role. Standard solar cell characterization methods do not reveal the contribution of individual nanowires. Techniques involving single nanowire lift-off after the working conditions, do not include the effect of the nanowire/substrate interface and generally demand a great deal of sample preparation. Hence, techniques where single nanowires can be probed directly on the growth substrate are advantageous.
In this work, we have developed a technique where a scanning tunneling microscope (STM)-probe is operated inside a scanning electron microscope (SEM) for characterization of the photovoltaic and electrical properties of single as-grown semiconductor nanowires. The SEM provides live imaging with nanoscale resolution while the piezo-controlled STM-probe contacts individual nanowires forming a closed electrical circuit. Reproducible ohmic contacts between the STM-probe and the nanowires were established through electron beam induced Pt deposition and Joule heating. Photocurrent measurements were enabled by mounting a light emitting diode (LED) in the SEM chamber. Current – voltage (I-V) measurements in both dark and illuminated conditions were performed on single GaAs nanowires with built-in radial p-n junctions. The best performing nanowire had an apparent power conversion efficiency of around 11 % under white LED illumination. Electron beam induced current (EBIC) maps were recorded to show the local charge separation ability within a nanowire with a spatial resolution of around 250 nm. Furthermore, the STM-probe was used to bend single nanowires, which affected the I-V characteristics. In conclusion, in situ STEM-SEM technique offers the possibility to investigate and compare the functional properties of individual as-grown nanowires that are part of a nanowire solar cell. The properties can be directly linked to the structure of the individual nanowires. This may play a key role in the further improvement of nanowire solar cells.

References:

CP03.04.22
In Situ Transient Absorption Spectroscopy During Materials Formation Cathy Y. Wong; University of Oregon, Eugene, Oregon, United States.

In situ diagnostics can yield fundamental insights into the materials formation process and aid in the design and optimization of materials for energy technologies, but in situ measurement has not been widely adopted for many time-resolved spectroscopic measurements. In particular, transient absorption (TA) spectroscopy can reveal the kinetic pathways of photoexcited species that dictate materials function, but TA is rarely performed in situ during materials formation. In TA a pump pulse photogenerates electronic excitations in the material, and the differential absorption caused by these excited species is measured by a probe pulse after a controlled delay time. The measurements at each delay time are typically collected in series, resulting in data acquisition times from many minutes to multiple hours. Many materials undergo formation processes on a shorter timescale than the data acquisition time for TA, precluding the accurate measurement of excited state dynamics in these systems. In this work, we introduce a novel implementation of transient absorption spectroscopy that can measure transients with up to a 60 ps pump-probe time delay in one shot. Data with an excellent signal-to-noise ratio can be acquired in just a few seconds. The measurement is validated by comparison to typical implementations of TA in static systems, and we report the results of in situ measurements during the formation of materials with applications in photovoltaics and light emitting devices. The information gained using this technique will be used to modify environmental parameters during the materials formation process to steer the material towards kinetically trapped states with excited state dynamics tailored for particular types of devices.

CP03.04.23
In Situ Studies of Ion Transport in Electrolyte and Electrolyte/Lithium Interfacial Reactions Yuan Yang; Columbia University, New York, New York, United States.

The interface of lithium/ electrolyte is critical to the performance of lithium metal anode and next-generation batteries. The interfacial reaction is affected by the metallic lithium, SEI together with ion transport in the electrolyte. While numerous studies have been carried out to study SEI and lithium metal, little attention has been paid to ion transport in the electrolyte, since it is extremely difficult to visualize. In this talk I will first discuss how to use an ultrafast Stimulated Raman Scattering microscope to visualize ion transport in the electrolyte, which illustrates positive feedback between ion concentration in the electrolyte and the growth of lithium dendrite. Besides visualizing ion transport in electrolyte, interfacial reaction between LATP ceramic electrolyte and lithium metal is also studied in-situ by TEM. We show that a BNA nanoscale coating layer is highly effective to prevent the side reaction between lithium and lithium metal. The impedance of Li/BN/LATP/Li cell only increases by 70% after 400 hours. In contrast, Li/LATP/Li cell impedance increase by three orders of magnitude after 400 hours. Consequently long term cycling is achieved in LiFePO4/LATP/Li metal battery with trace amount of PEO to wet the interface. The capacity retention reaches 95% over 100 cycles.

References:

CP03.04.25
Tracking the Underlying Redox Mechanism in Na2FePO4 Pyrophosphate Cathode for Sodium-Ion Batteries Ritambhara Gond and Prabeer Barpanda; Indian Institute of Science, Bangalore, India.

Rechargeable batteries presently govern the energy sector for potable electronics, hybrid vehicle and large scale grid storage devices. There are plethora of electrode materials have been reported to intercalate charge carrier species (Li, Na, K, etc.). 3d transition metal oxides, including layered LiCoO2, Li4Ti5O12, and olivine LiFePO4 exhibit good rechargeability and considered among the best cathodes for Li-ion batteries (LIBs). LiFePO4 has driven interest towards polyaminic materials for battery application due to its robust and safe cathode chemistry towards LIBs. There is no doubt that LIBs exhibit high energy density but due to its scarcity and non-uniform geographical distribution it needs to be complemented with similar chemistry. This has led researchers to find cheap and abundant material which is Na for large scale energy storage devices. Thus electrodes for Na-ion batteries (SIBs) need to be developed for sustainable energy storage. Which demands for more efficient, less hazardous and safer electrodes. In the race of developing novel and safer cathode material for LIBs and SIBs “pyrophosphate-based” polyaminic compounds has rekindled scientific attention.[1,2] Based on earth-abundant elements, Na2FePO4 and LiFePO4 can form an economic cathode for grid storage and other applications respectively. Among pyrophosphates, Na2FePO4 and LiFePO4 has been reported as a low cost cathode with promising electrochemical performance and thermal stability.[3,4] Na2FePO4 has triclinic (space group: P-1) and LiFePO4 has monoclinic (space group: P21/c) structure, where each corner of FeO6 octahedra is bridged to PO4 tetrahedra. In particular, in Na2FePO4 during the galvanostatic charge-discharge, reversible desodiation reaction occur between pristine Na2FePO4 and desodiated NaFe2+PO4 end-members involving an Fe3+/Fe2+ redox reaction. During this redox process, it goes through various mixed-valence intermediate compositions [Na2+xFe2-x+xPO4 , x = 0-1] followed by steady structural ordering/reorientation. These intermediate stages can be traced with a combination of electrochemical techniques and in-situ X-ray diffraction technology.[5] Here, in this present work the underlying redox mechanism has been studied by preparing a custom-made in-situ cell, able to perform both in reflection and transmission mode. Combustion made pristine Na2FePO4 was taken for the electrochemical testing which was prepared using Ferric nitrate (III) precursor. Carbothermal reduction was done using Ascorbic acid (for reduction of Fe3+ into Fe2+) and Urea fuel. Further, electrodes were prepared and Na half-cell was prepared using 1 M NaClO4 in PC as an electrolyte. In-situ X-ray diffraction patterns were recorded at C/25 rate during electrochemical testing. XRD pattern were recorded for 3624 seconds at an interval of 2 seconds in the angular domain of 9-60°. First peak coming at 10.78° 20 value corresponds to [010], and peak at 45.89° 20 value of [301] plane do not show any change during the sodium intercalation/ de-intercalation from Na2FePO4. Which reveals that these planes do not take part into charge carrier migration. Whereas, [011], [10-1], [01-1], [120] and [122] are the planes which reveals the extraction and insertion of Na-ion. Such observations simply tell the composition variation of Na into Na2FePO4 host during the galvanostatic charge-discharge process. Thus in the present paper we tried to study and track the changes made into the structure during the migration of charge species.

References:

CP03.04.26
Synchrotron-based soft x-ray spectroscopies, namely soft x-ray absorption (XAS) and emission (XES) spectroscopy, as well as their combination resonant inelastic soft x-ray scattering (RIXS) are powerful techniques to investigate the electronic structure of a variety of systems. We have intensively used these tools for the investigation of applied materials including thin-film solar cells, photoelectrochemical devices, batteries, ... (e.g., [1,2,3]). For these systems, in situ and operando studies are often required to answer the pertinent materials questions necessary for a further optimization of the respective device. Due to the photon-in-photon-out nature of XAS, XES, and RIXS with soft x-rays, it is, in fact, possible to investigate gaseous and liquid samples as well, making such in situ and operando investigations possible. However, since these spectroscopies and the corresponding synchrotron beamline environment usually require ultra-high vacuum (UHV) conditions, this requires the development of sophisticated experimental setups. In this presentation, we will discuss our recent progress in developing suitable environmental cells for in situ and operando soft x-ray studies. Showing selected examples, it will be presented how these techniques give insight into the electronic and chemical properties in the gas and liquid phase, as well as at liquid/solid interfaces. In many cases, the investigated materials are very sensitive to x-ray radiation, which requires careful experimenting with optimized approaches that will be discussed as well.


CP03.04.27
Systematic Design of High Performance Lithium-Sulfur Battery Using Efficient Polysulfide Adsorbent Porous Host Materials
Tilahun A. Zegeye; Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan.

Abstract

The need for large-scale energy storage, improved safety, and sustainable transport are driving research into alternative battery technologies with higher specific energies. Rechargeable Li-S batteries have high capacities (1675 mAh g\(^{-1}\)) and theoretical energy densities as high as 2600 Wh kg\(^{-1}\) making them promising candidates for the next-generation of energy storage systems. However, due to its insulating nature, polysulfide dissolution and poor cycle life, it has been challenging to achieve the existing technology requirement.

Herein we choose porous carbon as conducting agent and TiO\(_2\) nanotube as polysulfide adsorbent and forming hybrid nanostructured materials to overcome active material utilization and polysulfide dissolution problems. The porous host materials for sulfur was produced by a low cost, hydrothermal and annealing process with one step green synthesis approach. The process is facile, cheap, scalable and environmentally friendly. The material was characterized and examined by XRD, BET, XPS, SEM, TEM, Raman, TGA, CV, EIS and galvanostatic charge-discharge tests. It is found that the materials are highly porous and show both the characteristics of microporous and mesoporous behavior and contain large pore volume to impregnate large amount of sulfur. Moreover, the microporous carbon can effectively adsorb smaller sulfur (S\(_{2}\)) molecules in their narrow pores with increasing the electrical conductivity of the cathode by decreasing the resistance of sulfur and enhance active material utilization. Meanwhile, mesoporous carbon doped TiO\(_2\) nanotube were placed on the surface to prevent the overflow of sulfur as well as the dissolution of polysulfides in the electrolyte effectively and improve the strength of the entire electrode thereby enhancing the electrochemical performance. As a result, using the porous host-sulfur nanocomposite as a cathode material, we demonstrate excellent cycle stability with initial discharge capacity of 916 mA h g\(^{-1}\) with coulombic efficiency of over 98.6% at a current density of 0.2 C after 140 cycles.

Keywords: porous materials, lithium-sulfur battery, polysulfide adsorbent, cycle stability

SESSION CP03.05: X-Ray Diffraction and Batteries
Session Chairs: Ashfia Huq and Feng Wang
Wednesday Morning, April 24, 2019
PCC West, 100 Level, Room 101 C

8:30 AM *CP03.05.01
In Situ Synchrotron X-Rays Studies on the Synthesis of Energy Materials for Li-Ion Battery
Jianning Bai; Brookhaven National Laboratory, Upton, New York, United States.

Synthesizing new electrode materials with the desired phases and properties has often found difficult and mostly relies on trial and error since there are a variety of parameters that can have a strong influence on the structural properties (crystal structure, morphology, particle size), and eventually on electrochemical performance (e.g., capacity, rate capability, and durability) of the synthesized materials. Materials synthesis is such a complex process and often undertaken under non-equilibrium conditions, therefore posing a great challenge to theoretical predictions. In-situ, real-time tracking of the structural chemistry evolution during the synthesis reactions can provide details on reaction process, elucidating intermediate phases and how temperature, pressure, time and the precursor concentrations affect the kinetic reaction pathways. Synchrotron X-ray powder diffraction (SXPD), with its high beam intensity and angular resolution, allows in situ structural characterization in short time scales capable of catching subtle structural changes in the materials under synthesis. The presentation will introduce the in situ SXRD techniques developed at NSLS-II, as applied in the study of synthesis processes of cathode materials for Li-ion batteries. Specific examples on different materials and synthesizing methods will be given to show how the insights gained from in-situ studies may provide guidance to rational design and synthesis of new battery materials.

9:00 AM CP03.05.02
Large Area and Multimodal Study of Li-Ion Batteries with New In Situ Technologies
Stefanie Freitag; Zeiss, Munich, Germany.

In this study it was demonstrated that large area and multimodal in-situ lithium distribution studies and the comparison with the overall performance parameter enable an understanding of the context of batteries. It was shown in a first step that light microscopes allow a fast large area scan and in-situ dendrite grows observation in batteries. By means of an electron microscope with 61 electron beams (MultiSEM) it was then possible to image 1mm by 1mm large area with nanometer resolution, uncovering various material properties within the inspected region. New in-situ technologies like Raman, SIMS and TOF-SIMS laid out correlations between different material conditions and the respective local lithium distribution. In addition, electron beam absorption current (EBAC) experiments allowed a surface resistance and absorption current measurement. These results give direct evidence for material ageing and/or process errors.

9:15 AM CP03.05.03
In Situ Probing of Anionic Redox in Li-Rich Layered Cathodes
Chong Yin\(^{1,2}\), Bao Qiu\(^{2}\), Jianning Bai\(^{2}\), Zhaoping Liu\(^{1}\) and Feng Wang\(^{1}\); \(^{1}\)Sustainable Energy Technologies, Brookhaven National Laboratory, New York, New York, United States; \(^{2}\)Brookhaven Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China; \(^{3}\)National Synchrotron Light Source II, Brookhaven National Laboratory, New York, New York, United States.

Lithium-rich layered oxides (Li\(_{2}\)M\(_{O}\), Li\(_{1+x}\)M\(_{2+x}\)O\(_{4}\), M=Ni, Co, Mn) are among the most promising high energy cathode candidates for next-generation Li-ion batteries, with excess capacity enabled by both cationic and anionic redox. However, activating anionic redox (AR) may cause voltage hysteresis and voltage decay and so rational design of Li\(_{2}\)M\(_{O}\) of controlled AR activity becomes crucial to practical application. In this presentation, we will present recent results from combined in situ Synchrotron X-ray scattering and absorption studies on the AR activity in Li\(_{1+x}\)M\(_{2+x}\)O\(_{4}\) under operating conditions. Findings from this study, particularly about correlation between AR activity and local structural ordering, along with its implication to rational design of LR layered oxide cathodes will be discussed.
Materials storing energy via alloying reaction are promising anode candidate in rechargeable lithium ion batteries due to their much higher energy density than current graphite anode. Among these materials, bismuth provides a high theoretical volumetric capacity of 3800 mAh/cm$^3$ when it alloys with Li$^+$ to form Li$_x$Bi. Yet, its further development has been hindered by the unclear alloying mechanisms with Li$. In this work, we carry out real-time study of the de-alloying kinetics of Bi nanomaterials working as a Li$^+$ anode combining both in situ synchrotron XRD and in situ TEM. In situ synchrotron XRD reflects the phase transition information of the ensemble of many Bi nanoparticles, while in situ TEM demonstrates the structural evolution of single Bi nanoparticle at both high spatial resolution and high temporal resolution. Both two methods reveal that the Li-Bi alloying is a two-step process featuring two two-phase reactions with formation of Li$_x$Bi as the intermediate phase. More importantly, our work reveals an energetically favorable lithiation pathway along Bi-(012) planes during the Bi-Li phase transition process, which is further theoretically understood by DFT calculations. The fundamentals discovered in this work are expected to further guide the design of Bi-based electrode materials for battery performance enhancement in the future.

High-Ni transition metal layered oxides are among the most promising cathodes for Li$^+$-ion batteries. Their electrochemical activity is largely determined by the cationic ordering in octahedra (i.e., the basic building units, BBUs, of the systems). Therefore, mechanistic understanding of how the BBUs are inherited from precursors and subsequently evolve into the desired ordering during synthesis, may provide guidance to preparation of high-performance high-Ni layered oxides. Herein, a multimodal in situ x-ray characterization approach is employed to investigate structural/chemical evolution at scales ranging from very long range to the local individual octahedral units during solid-state synthesis of LiNi$_{0.5}$Mn$_{0.5}$O$_{2}$/Co$_{0.5}$O$_{2}$. Real-time observation corroborated by first-principles calculations reveals a topotactic transformation throughout the entire process, during which the breaking and reconstruction of NiO$_6$ octahedra occurs, leading to Li/Ni mixing and ordering. Findings from this study shed light on designing high-performance layered oxide cathodes and, broadly, various functional materials through synthetic control of the constituent BBUs.

Neutron and synchrotron x-ray facilities are indispensable scientific resources and provide powerful instruments and experimental techniques for both fundamental and applied researches. Neutrons and X-rays interact with matter in different ways, thus are often used as complementary tools for studying materials at the electronic, atomic and molecular levels. We have been utilizing neutron and synchrotron techniques to investigate a variety of materials for energy storage applications. In this talk, we will discuss the difference and similarity of neutrons and synchrotron x-rays, and their complementary use in battery materials research. We will present our recent results on in-situ/operando characterization of advanced materials for rechargeable batteries, from material synthesis to characterization. We will also discuss some challenging issues in battery materials characterization.

Neutron and synchrotron X-ray studies provide a unique insight into the materials' properties that are not easily accessible by other conventional techniques. They can provide information on the atomic scale, the structure and dynamics of materials, and their changes under various conditions. In this talk, we will present examples from our recent work on battery materials. We will discuss the strengths and limitations of neutron and synchrotron techniques, as well as the challenges and opportunities in the field.

References
chemical-vapor-deposition process. The 3D Graphene gives not only conductivity to electrode but also the effect of controlling electric potential for inhibition of solid-electrolyte interphase formation. With these properties, a solid-electrolyte interphase forms on the outer surface of the graphene, while solid-electrolyte interphase-free nanowires enable fast electronic and ionic transport, as well as strain relaxation over 2000 cycles, with 84% capacity retention even at ultrafast cycling (>20C). Moreover, these anodes exhibit high rate capabilities with capacity retention higher than 88% at 80C (vs. the capacity at 1C).

11:30 AM CP03.06.04
Proving Structural Evolutions of Silicon Anode in an Advanced Li-Ion Batteries Using In Situ Synchrotron X-Ray Studies Sungwon Lee1, Sung Sik Lee1, Jaewook Lee2 and Randall E. Winters1; 1Argonne National Laboratory, Lemont, Illinois, United States; 2LG Chem Ltd, Daejeon, Korea (the Republic of).

A major limitation to the advanced lithium ion batteries with silicon based anode is the huge volume expansion during lithiation, which leads the breakdown of the electrode structure, a low initial columbic efficiency and capacity fading upon cycling. A number of approaches, such as downsizing the silicon structures, modifying the structures with nanowires or porous matrix or making SiC composites have been performed to reduce the volume expansion phenomena. However, several critical issues such as un-satisfactory cyclability and the capacity decay still could not be avoided despite the prolonged cyclic life of Si anode. In present work, a synchrotron radiation based x-ray spectroscopic techniques with in-situ/operando capabilities were conducted to elucidate the structural evolutions of silicon anode upon electrochemical reactions in real time. Mg-doped SiO/C anodes were employed as a target material since they have revealed the excellent capacity retention. The results demonstrate that in-situ/operando x-ray characterization techniques provide the unique information for understanding the real reaction mechanism.

11:45 AM CP03.06.05
The Visualization of Single Grain Evolution in Operando Cathode Materials with the Coherent Hard X-Ray Diffraction Lixu Li1, Ross Harder1, Yingying Xie2 and Evan Maxey1; 1Argonne National Laboratory, Lemont, Illinois, United States; 2Shanghai Jiao Tong University, Shanghai, China.

As the in-situ X-ray powder Diffraction has become a routine method to characterize the crystal structure of battery particles under operando condition, it reflects the assemble average of all fundamental particles in the X-ray illumination volume. However, the local behavior remains a mystery until Ulvestad et al. [1] first applied Coherent X-ray Diffractive Imaging on a single LiNi0.5Mn1.5O4 nanocrystal under operando condition. The application of the Coherent Hard X-ray Diffraction in Bragg geometry enable us to visualize the structural, morphological and strain field evolution of crystals in operando battery materials. Coherent multi-crystal diffraction provides collective information of tens of crystals that bridges the statistical and individual behaviors of battery particles. In this presentation, Coherent Hard X-ray Diffraction experiment is demonstrated with a layered cathode material under operando condition [2]. I will show in details the fundamentals of Coherent X-ray Diffraction, the sample screening, instrumentation, data acquisition and interpretation.


SESSION CP03.07: X-Ray Spectroscopy and Battery Related Materials
Session Chairs: Anatoly Frenkel and Jenny Lockard
Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 101 C

1:30 PM *CP03.07.01
X-Ray Spectroscopic Studies of Energy Storage Systems Mahalingam Balasubramanian and Jason Croy; Argonne National Laboratory, Lemont, Illinois, United States.

There is significant interest worldwide to develop new battery systems for transportation and grid-storage applications. Development of new transformational technologies will require tailoring advanced materials and incorporating additional chemical or electrochemical processes. Using X-ray absorption, X-ray emission, and X-ray Raman spectroscopy, we seek to capture the fine details of the redox behavior (electronic structure) and the complex local structure of battery materials under device operating conditions. Such studies provide unique insight to develop structure-property correlations that are important to predict long-term battery performance and also help tailor new novel materials with high energy and power densities and stable crystal structures. In this talk, we will discuss operando studies of battery systems performed at the Advanced Photon Source.

2:00 PM CP03.07.02
In Situ XAS Studies of Layered Double Hydroxide Catalysts for Electrochemical Oxygen Evolution Reaction Maoyu Wang and Zhenxing Feng; Oregon State University, Corvallis, Oregon, United States.

In the past decades, renewable energy storage and conversion systems, such as fuel cells, water electrolysis, and metal-air batteries, have attracted great attention. Oxygen evolution reaction (OER) is a key half reaction of water splitting to produce clean fuels. However, the sluggish kinetics of OER has significantly limited the performance and commercialization of such energy conversion devices. Up to now, the most efficient OER catalysts are still noble metal and metal oxides of Ruthenium (Ru) and Iridium (Ir), which are not cost-effective catalysts and unstable under high potentials. Recently, single atom catalysts have been used to improve the surface-to-volume ratio to increase OER catalytic activity. In our work, we used layered double hydroxides (LDH) known as anionic or hydroxolate-like clays, which are inexpensive but are good catalysts or support for single atom catalyst to exhibit much improved OER activity. In particular, we utilized in situ XAS to identify the catalytic active centers. In our in situ works also provide insights into the mechanism of these catalysts during OER.

2:15 PM CP03.07.03
Laboratory-Based Hard X-Ray Photoelectron Spectrometer for the Study of Advanced and Complex Materials Anna Regoutz1, Manfred Mascheck2, Tomas Wiel1, Susanna Eriksson1, Cristopher Liljenberg1, Kornelius Tetzner1, Benjamin A. Williamson3, David O. Scanlon4 and Paul Palmgren1; 1Imperial College London, London, United Kingdom; 2Scienta Omicron, Uppsala, Sweden; 3University College London, London, United Kingdom.

The success of material discovery and engineering is partly based upon the development and application of highly advanced characterisation methods. Hard X-ray photoelectron spectroscopy (HAXPES) has traditionally found its application in the core topics of condensed matter physics, but the slowly growing number of beamlines worldwide has widened its appeal to other interest groups. HAXPES uses x-rays in the 2-10 keV range to excite photoelectrons, which are used to non-destructively study the chemical environment and electronic structure of materials. As its soft X-ray counterpart (SXPS or simply XPS) it delivers qualitative and quantitative information on elemental distributions, chemical states, and electronic structure.

In contrast to the very surface-sensitive XPS, HAXPES is much more bulk sensitive. This makes it applicable to bulk materials and structured samples, e.g. layered samples and heterostructures. In addition, its bulk sensitivity means that realistic experiments can be investigated without the need of prior surface preparation. Furthermore, results can easily be correlated to a whole range of other bulk-sensitive characterization results, and therefore to structural information and material properties. However, the number of existing HAXPES systems is very small and they are predominantly located at synchrotrons (approx. 20 beamlines worldwide) due to low photonization across sections necessitating high X-ray intensities, limiting their availability to users and applications.

This work presents a new laboratory-based instrument capable of delivering monochromated hard x-rays with an energy of 9.25 keV and a focused 30x45 μm² X-ray spot, giving excellent energy resolution of <0.5 eV. Systematic reference measurements are presented outlining the systems capability, including energy resolution, X-ray and signal intensity, and stability. Results from a rutile TiO₂ bulk sample show the wide range of possible signals that can be collected, such as shallow and deep core levels, Auger lines, and valence bands. The valence band measurements are benchmarked against theoretical results from density functional theory. Furthermore, pure bulk measurements a range of metal oxide
ultimately, this spectrometer presents an alternative to synchrotron-based endstations and will help to expand the number and range of HAXPES experiments performed in the future. HAXPES is a cutting edge characterisation method and the advancement of this technique will tremendously increase the potential to study an ever increasing range of inorganic materials and beyond.

2:30 PM BREAK

SESSION CP03.08: X-Ray Spectroscopy and Catalysis

Session Chairs: Mahalingam Balasubramanian and Markus Winterer

Wednesday Afternoon, April 24, 2019

PCC West, 100 Level, Room 101 C

3:30 PM CP03.08.01

In Situ Determination of Active Species and Active Sites in Water Gas Shift Reaction Over Pt/\text{CeO}_2 Catalysts

Yuyuan Li\textsuperscript{1}, Matthew Kottwitz\textsuperscript{2}, Ralph Nuzzo\textsuperscript{3} and Anatoly Frenkel\textsuperscript{1,3}; \textsuperscript{1}Materials Science and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; \textsuperscript{2}Chemistry, Brookhaven National Laboratory, Upton, New York, United States.

Determining the structure of active species and active sites, and their evolution in reaction conditions is a required step towards understanding catalytic mechanisms. In heterogeneous catalysts, multiple species of the same element: single atoms, larger clusters and nanoparticles may appear, disappear and coexist during the reaction. There is therefore a strong need to monitor the charge and geometry of metal centers, as well as their dynamic changes, in reaction conditions. Even with that capability achieved, the reaction mechanism may not be understood until it is known which species are catalytically active, and which ones – spectators. One possible way to address that is to combine multiple in situ probes that can resolve between the heterogeneously distributed species with the online product analysis. This combination will correlate the changes in the spectra (and thus – in the structure) with the changes in activity and thus help identify the active species during the reaction.

To illustrate these ideas, and highlight an exemplary application of this multimodal approach I will show how we treated the complexity of a newly synthesized and highly active selective oxidation catalyst, a model single atom catalyst formed by the dilute substitutional doping of Ceria by isolated Pt atoms, (Pt)\text{CeO}_2. Among the techniques chosen for its characterization, STEM probes the distribution of single atoms and nanoparticles in the sample, in situ XANES and EXAFS probe the local structure around metal atoms/ions, XPS and RIXS – their charge states, DRIFTS – surface composition, and online MS – product formation. We used this multimodal approach to reveal the correlation of the number of Pt\textsuperscript{4+} ions in Pt/\text{CeO}_2 catalysts with the observed change in the water-gas shift reaction activity—data definitively establishing that Pt nanoparticles formed during the reaction, and not the Pt single atoms, are the active species. The Pt atoms on the nanoparticle perimeter with proximate Ceria bonding interactions comprise the catalytically active sites.

This work was supported by U. S. Department of Energy, Office of Basic Energy Science under Grant No. DE-FG02-03ER15476

4:00 PM CP03.08.02

Unveiling Site-Selective CO Disproportionation Mediated by Electron Beam Excited Localized Surface Plasmon Resonance

Wei-Chung D. Yang\textsuperscript{1,2}, Canhui Wang\textsuperscript{1,2}, Henri J. Lezec\textsuperscript{1} and Renu Sharma\textsuperscript{1}; \textsuperscript{1}Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; \textsuperscript{2}Maryland NanoCenter, University of Maryland, College Park, Maryland, United States.

Optically-excited localized surface plasmon (LSP) resonances have been used to induce chemical reactions, such as hydrogen dissociation, water splitting, and ethylene epoxidation\textsuperscript{1}. Energy harnessed by plasmonic nanostructures and transferred to adsorbed reactants on nanostructure surfaces initiates chemical processes that compensates for the thermal energy required otherwise. However, sub-particle level information, regarding the relevant LSP resonance modes and their response to reactants, has not been identified by variants of optical spectroscopy.

Herein, we use a focused electron beam in an environmental scanning transmission electron microscope (ESTEM) to excite LSP resonances on triangular Au nanoparticles on TiO\textsubscript{2} support to drive CO disproportionation at room temperature (commonly driven by thermal energy at 400 °C to 600 °C), and the carbon product labels the catalytically active site at the sub-particle level. ESTEM, operated at 80 kV and equipped with a monochromated electron source with an energy resolution of 0.08 eV, was used to acquire in situ low- and core-loss electron energy loss spectroscopy (EELS) maps to spatially resolve both LSP mode distribution (low-loss EELS) and gas adsorption sites (core-loss EELS) on a Au nanoparticle by comparing the data collected in vacuum and CO environment. The optimal electron beam position to excite specific LSP resonance modes on the Au nanoparticle can be identified by applying the non-negative matrix factorization (NMF) to a low-loss scanning transmission electron microscopy (STEM) EELS map\textsuperscript{2}. We found a dipole mode that resulted in the maximum LSP electric field can be excited by placing electron beam at an aloof position outside the cantilevered nanoparticle corner (near-field excitation). This dipole mode displayed a spectral blue-shift in the presence of CO (P\textsubscript{CO} = 110 Pa) and returned to the original resonance energy when CO is evacuated. More importantly, STEM cathodoluminescence (CL) measured simultaneously with EELS allowed us to probe the scattering from the Au nanoparticle in either vacuum or CO environment, which can be used to apprehend the absorbed energies by the Au nanoparticle during the LSP induced chemical process.

A core-loss STEM-EELS map acquired at P\textsubscript{CO} = 110 Pa, showed increased carbon K-edge signal at the selective locations on the nanoparticle edges, which can be related to CO adsorption. By either raster-scanning an electron beam over the Au nanoparticle or deliberately placing it statically at an optimal near-field excitation position in CO environment, the electric field of excited LSP mode can drive disproportionation of the adsorbed CO molecules in the vicinity and deposit amorphous carbon at the cantilevered corner. The location of carbon deposit suggests that the catalytically active sites on Au nanoparticles are those where preferred CO adsorption sites and locations of maximum LSP electric field magnitude (resonance antennas) superimpose. Our findings provide, for the first time, detail experimental information on sub-particle localization of plasmonic catalysis with nanometer scale precision and possible guidelines to develop antenna based plasmonic catalysts.

References

4:15 PM CP03.08.03

X-Ray Absorption Study on Iron(III)Acetylacetone Vapor and Nanoparticles Produced from It

Oleksandr Levish and Markus Winterer; Nanoparticle Process Technology, Universität Duisburg-Essen, Duisburg, Germany.

Iron containing nanoparticles exhibit a broad spectrum of applications due to a large variety of chemical (e.g. redox potential) and physical properties. Those are highly depending on the oxidation state and crystal structure. Different phases and morphologies can be achieved by changing the nanoparticle synthesis parameters [1]. Chemical vapor synthesis (CVS) is a technique which enables reproducible synthesis of nanoparticles with reliable control of synthesis parameters. Organometallic compounds are used to introduce metals into CVS reactor. Solid precursors offer easier handling, mostly lower toxicity and are advantageous for adjusting gas redox potential through a higher carbon content. Iron(III)acetylacetone (Fe(acac)\textsubscript{3}, Fe(C\textsubscript{5}H\textsubscript{7}O\textsubscript{3})\textsubscript{3}) is such solid precursor used for CVD (chemical vapor deposition) and CVS to generate iron containing nanoparticles. However, due to a higher molecular mass and intermolecular interaction, the volatility of Fe(acac)\textsubscript{3} is relatively low, still it needs to be sublimated to deliver it as vapor to CVD and CVS processes. In fact, only little is known about the local and electronic structure of Fe(acac)\textsubscript{3} vapor.

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In this study we designed a novel vapor cell for measuring vapor species in the gas phase. With this vapor cell Fe(acac)$_3$ vapor is successfully provided for XAS (X-ray Absorption Spectroscopy) measurements under fluorescence detection. We investigate Fe(acac)$_3$ vapor in-situ at the Fe-K edge using the vapor cell at conditions close to those in the reactor. We compare these data to solid Fe(acac)$_3$ and Fe(acac)$_3$ in solution (water, isopropanol and acetone). Additionally, we investigate nanoparticles made from Fe(acac)$_3$ under different synthesis conditions by XAS. This enables a better understanding of processes occurring in the CVS systems using iron as a probe.


Acknowledgment:
DFG (German Research Foundation)
DLS (Diamond Light Source), DESY (Deutsches Elektronen-Synchrotron), APS (Advanced Photon Source) for providing beamtime

4:30 PM *CP03.08.04
In Situ X-Ray Absorption Spectroscopy Studies of Catalysts in Electrochemical Reactions Zhenxing Feng; Oregon State University, Corvallis, Oregon, United States.

Electrocatalysis plays a key role in producing/converting molecular energy carriers and metal to either store electricity from solar or wind energy in chemical forms or produces electrical energy through fuel cells and metal-air batteries. In the search of highly efficient electrocatalysts, it is important to understand how catalysts work, then subsequently a rational design rule can be provided. We use several in-situ synchrotron X-ray techniques, particularly X-ray absorption spectroscopy (XAS), to probe the element-specific changes from heavy metal (e.g., Mn, Co, Fe, etc) to light element (e.g., O, N) during various electrochemical reactions including CO$_2$ reduction and oxygen evolution/reduction reactions. We not only directly observe how catalysts adjust their local structures and valence state to promote reactions, but also identify different reaction centers that weren’t considered before and couldn’t be found from ex situ experiments. In my talk I will show couple of cases to highlight the importance of our in situ studies as well as new thoughts for catalyst designs.

SESSION CP03.09: Small Angle Scattering, Ion Scattering and Related Methods
Session Chairs: Jianming Bai and Feng Wang
Thursday Morning, April 25, 2019
PCC West, 100 Level, Room 101 C

8:30 AM *CP03.09.01
Exploring Pore Formation of Atomic Layer-Deposited Overlayers by In Situ Small Angle X-Ray Scattering Tao Li1,2,1; Argonne National Laboratory, Downers Grove, Illinois, United States; 2Chemistry & Biochemistry, Northern Illinois University, DeKalb, Illinois, United States.

In this presentation, we explore the pore structure of overcoated materials by in situ synchrotron small-angle (SAXS) and wide-angle X-ray scattering (WAXS). Thin films of aluminum oxide (Al$_2$O$_3$) and titanium dioxide (TiO$_2$) with thicknesses of 4.9 and 2.5 nm, respectively, are prepared by atomic layer deposition (ALD) on nonporous nanoparticles. In situ X-ray measurements reveal that porosity is induced in the ALD films by annealing the samples at high temperatures. Moreover, this pore formation can be attributed to densification resulting from an amorphous to crystalline phase transition of the ALD films as confirmed by high-resolution X-ray diffraction and the pair distribution function. Simultaneous SAXS and WAXS results show not only that the porosity is formed by the phase transition but also that the pore size increases with temperature.

9:00 AM CP03.09.02
In Situ Small-Angle X-Ray Scattering Observation of Electrophoretic Deposition at the Nanoscale Viktor Mackert and Markus Winterer; Nanoparticle Process Technology, Universität Duisburg-Essen, Duisburg, Germany.

Electrophoretic deposition (EPD) is a colloidal forming process which may be described by two steps: (1) migration of charged particles in an electric field due to electrophoresis and (2) deposition on a substrate working as electrode. Nevertheless, due to a lack of in-depth mechanistic understanding of the film deposition and formation process control of the film microstructure remains still a challenge. Generally accepted is that particle agglomeration plays an important role during deposition. Recent studies investigated ligand-stabilized nanoparticles in organic solvents during EPD with small-angle X-ray scattering [1, 2]. We investigate the EPD process of chemical vapor synthesized (CVS) SnO$_2$ nanocrystals. Purely electrostatic stabilized colloidal SnO$_2$ nanocrystals in aqueous media are deposited on silicon anode due to their high negative charge in an X-ray transparent liquid EPD cell. We use synchrotron radiation based small-angle X-ray scattering (SAXS) in situ in the near electrode region. This approach allows to study structural changes like radius of gyration, fractal dimension at the nanoscale during EPD by probing locally with high spatial resolution (nanobeam) time dependent at the local electrode environment (200 – 3200 nm).


Acknowledgement:
Deutsches Elektronen-Synchrotron (DESY) for beamtime allocation

9:15 AM CP03.09.03
Advanced Setups for In Situ Growth and Characterization of Materials by Ion Beams Tuan T. Tran1, Barbara Bruckner1, Karim Kantre2, Marcos Moro2, Mauricio Sortica2, Silma Correa1, Svendja Lohmann1, Valentina Paneta1 and Daniel Primetzhofer1,2; 1Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden; 2Tandem Laboratory, Uppsala, Sweden.

The Ion Physics group and the Tandem laboratory at Uppsala University have recently developed substantial infrastructure for in-situ film deposition, modification and high-resolution characterisation using ion beam-based methods, by set-ups located at three separate accelerators: a 5 MV Pelletron Accelerator, a 350 kV ion implanter/medium-energy-ion-scattering (MEIS) system and a 10 kV Time-of-Flight low-energy-ion-scattering (ToF-LEIS) system. For example, the 6th beam line of the Pelletron Accelerator features an analytical chamber equipped with a triple-electron-beam evaporator, an ion source used for sputtering, a solid state detector, an X-ray detector and a pure germanium detector used for a series of ion beam characterisation techniques: Rutherford backscattering spectrometry (RBS) providing depth profiles of targets constituents with down to 20 nm depth resolution, nuclear resonance analysis (NRA) and particle-induced X-ray emission (PIXE). Additionally, different gases, such as hydrogen and oxygen, can be introduced into the chamber during thin-film growth or beam exposure [1]. The sample temperature can be controlled from cryogenic levels up to typical values 600 °C during or after the growths. A fully independent load-lock chamber can be detached and transferred to the MEIS system for further analysis without exposing the film to air. For the MEIS system, the operational energies range from 20 kV to 350 kV, enabling high-resolution near surface analysis [2]. Scattering data can be acquired by two independent ToF-position-sensitive detectors. One system features a large solid angle (0.25 sr), suitable for acquisition of blocking pattern permitting to study depth-resolved crystallographic properties in real space. The other detector features smallersolid angle (0.02 sr), but is situated at larger distance from the sample in order to achieve superior depth resolution (typically ~5 Å). The sample holder can be heated up to 600 °C for in-situ annealing experiments. Finally, for the LEIS system, the main analytical potential is to grow and investigate ultra-thin films in a regime very close to the sample surface (few monolayers). An ultra-high vacuum sample preparation chamber connected to the LEIS system features a triple-electron-beam evaporator, an annealing stage, a sputter gun mainly used for surface cleaning prior the measurements, low-energy-electron-diffraction and Auger electron spectroscopy.

Reference
Cluster Tool for In Situ Processing and Comprehensive Characterization of Energy Materials at High Temperatures Matthias Kräuse1, Robert Wenisch1, Frank Lungwitz1, Irene Hera2, Daniel Janke1, Ibon Azkon1, Ramon Escobar Galindo3 and Sibylle Gemming1, 3. 1 Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany; 2 Department of Applied Physics, University of Salamanca, Salamanca, Spain; 3 IMEMYAT, Universidad de Cádiz, Puerto Real, Spain; 3 Technische Universität Chemnitz, Chemnitz, Germany.

In situ processing and comprehensive characterization is essential for design and development of materials used and processed at high-temperatures. Here, a new cluster tool for processing and depth-resolved compositional, structural and optical characterization of layered materials with thicknesses ranging from sub-nanometer up to 1000 °C is described [1]. The implemented techniques comprise magnetron sputtering, ion irradiation, Rutherford backscattering spectrometry, Raman spectroscopy and spectroscopic ellipsometry. The combination of techniques enables sample processing by cold, clean, waste-free, and industry-relevant technologies, quantitative depth-profiling for elements with z ≥ 6, structural and chemical characterization, sensitivity and nm-precise thickness and optical information for single layers, multilayers and composites. In this study, the cluster tool was used for i) metal-induced crystallization with layer-exchange of a-Si/Ag layer stacks, and ii) for high-temperature characterization of two types of solar-selective coatings for concentrated solar power (CSP), namely Al,Ti,(O,N)x-y (O,Ru)z single and multilayer [2, 3] and an n-type doped solar-selective transparent conductive oxide [4]. Starting with an a-Si/Ag bilayer stack, metal-induced silicon crystallization with partial layer exchange occurs at about 540 °C. The final stack is approximately described by the sequence crystalline Si (c-Si)/Ag/c-Si. All the layers contain minor fractions of the other elements. Moreover, the Si volume fraction comprises approximately 10 % of amorphous Si. For the CSP coatings, no compositional and structural changes were found up to a maximum temperature of 840 °C in vacuum. Both types of solar-selective coatings thus represent promising materials for the next generation of CSP technology.

With theoretical specific capacity of 1672 mAh/g and specific energy of 2600 Wh/kg and practical specific energy of 500 Wh/kg demonstrated recently, values that are highest among all solid elemental redox couples, rechargeable Li-S batteries are regarded as the next step in emerging “green” electrical energy storage technology revolution to replace Li-ion batteries [2020-2025] for applications in transportation (EVs), national security (UAV, UGV), communications, potable electronics, etc. Produced using abundant, environmentally friendly nontoxic materials, light-weight high-energy density Li-S batteries also offer the possibility of significantly reduced cost. The continuous quest for better, high-performance batteries is currently targeting novel Li-S chemistries, shifting R&D efforts towards battery architectures with optimally engineered functional interphases which offer longer cycle life and high rate capabilities. Despite recent advances, more efforts should be applied to achieve the requisite performance, lifetime and reduced cost needed for new battery technologies to enter the market.

For a long time, practical implementation of Li-S technology has been hindered by poor rate capability and short cycle life due to deleterious effects caused by Li polysulfide redox processes. In the past, new battery technologies to enter the market. For a long time, practical implementation of Li-S technology has been hindered by poor rate capability and short cycle life due to deleterious effects caused by Li polysulfide redox processes. In the past, new battery technologies to enter the market. For a long time, practical implementation of Li-S technology has been hindered by poor rate capability and short cycle life due to deleterious effects caused by Li polysulfide redox processes. In the past, new battery technologies to enter the market. For a long time, practical implementation of Li-S technology has been hindered by poor rate capability and short cycle life due to deleterious effects caused by Li polysulfide redox processes. In the past, new battery technologies to enter the market.
highly-localized Angstrom-scale source to locally excite molecular vibrational resonances. Plasmonic nanoparticles amplify the process and enable molecular-scale Raman mapping. Finite difference time domain simulations of molecule-decorated gold nanorods show that laser pump intensities less than 3mW/µm² can locally enhance the Raman peak, with sub-2nm resolution of molecular fingerprints. Experimentally, we synthesize colloidal gold NRs functionalized with 4-Nitrophenol (4NTP) as a Raman reporter. Upon electron beam excitation of the nanorod plasmon modes, we observe a ten-fold increase in the Raman intensity of the 1335cm⁻¹ and 1579cm⁻¹ lines of the 4NTP molecule. Monochromated electron energy loss spectroscopy (EELS) confirms the plasmon modes we excite during each individual Raman acquisition. Combined, our results promise high-resolution mapping of ionic and molecular transformations, en-route to site-selective and product specific photocatalysis.

11:00 AM CP03.10.02
Boron Nitride Nanotube Electron-Beam Induced Oxidation at 80keV Hsin-Yun Chao¹, ², Dmitri Golberg¹, ², Cheol Park¹, Renu Sharma³ and John Cumings¹; ¹Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ²Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia, United States; ³School of Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, Queensland, Australia; 4Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Boron nitride nanotubes (BNNT) are superlative mechanical properties, promise as a possible structural material. The most demanding applications include lightweight components for space vehicles and radiation shielding. In these environments, carbon nanotubes (CNT) have been shown to be affected by ionizing radiation, which diminishes the desirable properties. Boron nitride nanotubes (BNNT) are an analogous structure with similar mechanical properties to CNT, but with more uniform electronic properties. Here, we present results from beam damage experiments with in-situ environmental transmission electron microscopy (ETEM). Oxygen pressures introduced vary from 10⁻² Pa to 10⁻¹ Pa and an electron beam dose from 10² e/nm²-s to 10 e/nm²-s. Our observations show BNNT to have more than one order of magnitude higher resistance to oxidation under the electron beam than that of CNT at comparable oxygen pressures. This demonstrates BNNT as a competitive alternative to CNT with enhanced performance in extreme energetic environments.

11:15 AM CP03.10.03
Advanced In Situ and Ex Situ S/TEM Probing of Interfacial Process in Rechargeable Batteries Chongmin N. Wang; Pacific Northwest National Laboratory, Richland, Washington, United States.

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced battery performance. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM and in-situ liquid SIMS for probing into the structural and chemical evolution of energy storage materials. Both ex-situ and In-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed. Most importantly, integration of different analytical tools appear to be the key for capturing complementary information.

11:30 AM CP03.10.04
Cu₂O Island Growth Process During Cu(100) Oxidation Revealed by Correlated In Situ Environmental TEM and Multiscale Simulations Meng Li, Matthew T. Curnan, Wissam A. Saiidi and Judith C. Yang; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

When exposed in oxidizing environment, most metals and alloys will form surface oxide, which causes problems like corrosion and degradation, but could also be used in applications like catalysts and transistors. With the increasing application demands toward the nanoscale, fundamental understanding of the microscopic mechanisms of surface oxidation is essential for the prevention, prediction and controlled growth of metal oxide. The process of surface oxidation is usually divided into three stages, namely oxygen chemisorption, oxide nucleation and growth, and bulk oxide growth. Among these three stages, the initial stage, which spans from the start of oxygen chemisorption to surface reconstruction and the onset of oxide nucleation, is the least understood regime of oxidation, as it is inaccessible to traditional surface science and bulk material science experimental methods. Current computational capabilities and theoretical modeling are still unable to encompass oxide nucleation due to the large computational expense required to simulate nucleation over sufficiently large time and size scales.

In this work, by combining in situ Environmental TEM (ETEM) and multiscale atomistic simulation, we explore the dynamic processes of the initial stages of Cu(100) oxidation. By in situ oxidizing Cu thin films inside the Hitachi H-9500 ETEM (300 kV, LaB₆, with homebuilt gas delivery system with up to 3 lines of gas injection) with flowing O₂ gas, the initial stages of oxidation were investigated. The dynamic process from surface reconstruction to oxide nucleation and growth was observed, delimiting the initial oxidation stage threshold at which ETEM can effectively discern dynamic processes. Previous works by Zhou et al reported that the first CuO layer during Cu(100) oxidation grows along the (100) surface from a 2-atomic layer wetting layer. However, our work found the ensuing 3D CuO island grows in a layer-by-layer adatom growth mechanism along the CuO(110) direction. To better understand the observed phenomenon, a multi-scale computational approach was applied. The dynamic and energetic changes during CuO/growth under O₂ were calculated. A preferential monolayer formation of CuO monolayer along CuO(110) was found to be the reason. This correlated in situ ETEM and multiscale simulation method forms a feedback loop between ETEM results and simulations that allows computational and experimental results to validate and support one another, and helps to fundamentally explain oxide nucleation preference as function of orientation, defects (such as steps), temperature and pressure, and other environmental factors. Our results will enhance the understanding of surface oxidation and will also provide insights into understanding initial oxide growth mechanisms of other metal/alloy systems.

Acknowledgment
The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, NSF DMR-1508417, and DMR-1410335, as well as support from Hitachi-HighTech and technical assistance from the Nanoscale Fabrication and Characterization Facility (NFCF) in the Petersen Institute of Nano Science and Engineering (PINSE) at the University of Pittsburgh.

11:45 AM CP03.10.05
Real-Time Imaging of Reducible Oxide Nanoparticle Surface Reconstructions Using Time-Resolved Aberration-Corrected Transmission Electron Microscopy Ethan L. Lawrence¹, Ramabhy D. Levin¹, Benjamin K. Miller² and Peter Crozier¹; ¹Arizona State University, Tempe, Arizona, United States; ²Gatan, Inc., Pleasanton, California, United States.

The surface atomic arrangements of reducible oxides govern their oxygen exchange properties, and the ability to control and optimize structural parameters is of crucial importance for many applications, in particular in heterogeneous catalysis and photocatalysis [1]. Characterizing the structural evolution of catalyst nanoparticle surfaces with high spatial and temporal resolution may enable differentiation between functionally-relevant active structures and passive spectator structures, both of which may change during a single reaction “turnover” event. Aberration-corrected transmission electron microscopy (AC-TEM) has been used extensively to study nanoparticle surface dynamics using in situ imaging techniques [2]. Recent advances in imaging technology, namely direct detection cameras with fast acquisition modes, have enabled many new materials phenomena to be investigated. Additionally, with the advent of fast image acquisition, advanced processing techniques are essential for extracting useful information from large, often noisy image datasets. In this work, we use time-resolved AC-TEM to characterize oxygen-exchange induced surface reconstructions on CeO₂ nanoparticles, a reducible oxide that is used extensively in catalysis applications due to its oxygen exchange properties [1].

An aberration-corrected FEI Titan ETEM equipped with a Gatan K2 IS direct detection camera (with high detection quantum efficiency) was used to image CeO₂ nanoparticles at 400 frames/second and 10⁶ eÅ⁻²s⁻¹ with a pressure of <10⁻⁶ Torr at the sample for ~30 seconds. Due to the fast acquisition rate, large datasets were acquired and individual 1⁴⁰⁰ second exposure frames were obtained with signal-to-noise. To reduce noise in each individual frame, images were spatially binned and a Gaussian blurring filter was applied. MIPAR, a commercially available software with a recipe-based image processing method, and custom-written MATLAB codes were used to identify Ce atomic column positions and quantify column intensities in large datasets [3]. The integrated intensity quantization of each atomic column and AC-TEM image simulations were used to determine the number of Ce atoms within each column and track atomic migration at the surfaces. We observe dynamic surface reconstructions and lattice expansions/contractions associated with oxygen vacancy creation and annihilation. Further results providing insight into structure-dependent properties of oxygen exchange reactions on reducible oxides will be presented [4].


**SYMPOSIUM CP04**

**Interfacial Science and Engineering—Mechanics, Thermodynamics, Kinetics and Chemistry**

April 22 - April 26, 2019

Symposium Organizers
Fadi Abdeljawad, Clemson University
Julie Cairney, The University of Sydney
Timothy Rupert, University of California, Irvine
Jason Trelewicz, Stony Brook University

* Invited Paper

**SESSION CP04.00: Late News in Interfacial Science and Engineering**

Session Chairs: Jessica Krogstad and Timothy Rupert

Monday Afternoon, April 22, 2019

PCC North, 100 Level, Room 124 A

**1:30 PM CP04.00.01 Solute Segregation and Grain Boundary Transport in Nanocrystalline Alloys—Insight from Diffusion Triples**

Pralav Shetty, Caelin Muir and Jessica A. Krogstad

Materials Science and Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois, United States; Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Solute segregation in nanocrystalline metals has been widely explored as a route to improve the thermal stability of fine grain microstructures. Efforts have revealed that segregation may not always be uniform or subtle, thereby shifting the microstructural stabilization mechanism [1,2]. Delineating the subtle differences between these two mechanisms maybe be possible through improved understanding of mass transport along solute decorated grain boundaries. In this work, we present very recent observations of grain boundary diffusion with concomitant microstructural evolution by employing a thin film diffusion triple configuration. A 10nm layer of pure Al then a 50nm layer of a nanocrystalline, highly textured Ni-Cr alloy are deposited via DC magnetron sputtering on to a coarse-grained Ni-Cr alloy substrate of the same nominal composition. These diffusion triplets are annealed under flowing Ar at 600°C and the asymmetric diffusion profile is extracted via STEM EDX and APT characterization. Comparison of these diffusion data are presented against similar thin film diffusion triplets containing ~1at% V in the nanocrystalline films. Despite nearly identical initial microstructures, there are significant differences between these diffusion profiles, with implications for microstructural stability as well as environmental resistance.


**1:45 PM CP04.00.02 Surface Energy Interactions in Crystalline Coffee Rings**

Samantha McBride, Rachael S. Skye and Kripa K. Varanasi; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The coffee-ring effect refers to the phenomena in which a drop of a colloidal suspension evaporates on a substrate and deposits an ordered ring-structure due to the outward radial evaporative flow. This phenomena has been well-investigated due to numerous practical applications including ink-jet printing, microscale separations, and sensing/diagnostics. However, the phenomena has been less quantified for a crystallizing solution. When a drop of salt solution is evaporated, the salt becomes supersaturated and crystals begin to emerge at the substrate. The emerging crystals alter the local wettability of the substrate, and fundamentally alter fluid dynamics of evaporation, which in turn alters the form of deposit left behind. Here, we investigate the role of energetic interactions between the substrate, crystals, and solution. We systematically vary the substrate interfacial chemistry by deposition of silane groups of various surface energies, and use four different crystal systems to probe this effect. We find that crystals with favorable interactions with the underlying substrate chemistries alter deposit morphology, while non-interacting crystals behave similarly to colloidal particles, and develop phase diagrams predicting this behavior. These results can be used for fine-tuned control and understanding of crystalline evaporative deposits.

**2:00 PM CP04.00.03 Evolution of Persistent Metastable Phases During Mg Metal Corrosion**

Vaithiyalingam Shuathanandan, Abraham Martinez, Peter V. Sushko, Arun Devaraj, Olga Marina, Vineet Joshi, Suntharanpillai Thevuthasan and Vijayakumar Murugesan; Pacific Northwest National Laboratory, Richland, Washington, United States.

Magnesium metal is a potential candidate for high strength to weight ratio alloys with wide application in aerospace and automotive industries. However, poor corrosion resistance under ambient environmental conditions is the bottleneck for industrial deployment. Designing passivation layers and/or corrosion resistance alloys require fundamental understanding of the corrosion process. The traditional ex-situ spectroscopic measurements of polycrystalline metal surface with ubiquitous surface impurities provided indistinct view of the corrosion process. To clearly distinguish the mechanism and sequence of corrosion process, we employed in-situ cryo-based x-ray photoelectron spectroscopy (XPS) measurements on well-defined pure and aqueous solution exposed Mg single crystal surfaces in combination with ab initio atomistic modelling studies. Clean Mg (0001) surfaces were carefully exposed to pure and sodium chloride mixed water and the subsequent interfacial reactions were studied through integrated experimental and theoretical approach. This study provides atomistic view of magnesium hydroxide nucleation as main product of the corrosion process. Under salt conditions, the competitive nucleation process between magnesium hydroxide and magnesium chloride were observed along with the formation of magnesium chloride hydrate and magnesium hydroxide hydrate phases. By combining the energy requirements from computational modelling and the electronic states of corrosion products, the mechanism and sequence of corrosion process on Mg metal will be discussed.

**2:15 PM CP04.00.04**

The increasing research of nanowires (NWs) as building blocks for electronic, optoelectronic, energy devices and quantum computing is driven by the unique physical, and chemical properties originate from their nanoscale dimensionality. Catalyzed surface-guided NWs offer the possibility to control their position, direction and crystallographic orientation, which eventually leads to high-performance devices. To adequately control these features and gain predictive abilities, a deeper understanding of the growth mechanism of surface-guided NWs is required. Here, we experimentally and theoretically study the kinetics of planar catalyzed NWs. A model is presented that considers two main regimes of the growth rate of NWs depending on their thickness: the Gibbs–Thompson regime, which dominates the growth of thinner NWs, and the surface-diffusion-induced regime, which dominates the growth of thicker ones. By developing this kinetic model and fitting it to the experimental kinetic data, we determine the dimensionality of the surface diffusion. We observe a good correlation between the model and the results for surface-guided ZnSe and ZnS NWs grown on sapphire. The dimensionality of the surface diffusion value was determined to be ~1.5 and ~1.8 for ZnSe and ZnS NWs, respectively, in contrast to the value of 1 for vertical NWs growth models, supporting the difference between the two growth morphologies. The newly developed model distinguishes between the growth mechanisms of horizontal and vertical NWs, underscores the important role of the substrate in the horizontal growth, and provides new insights into the mechanism of surface-guided NWs growth. Understanding the growth mechanism introduces the possibility of controlling the growth directions and crystallographic orientations of the aligned NWs accurately and helps gain some prediction abilities of the NWs properties, leading to better nanowire-based electronic and optoelectronic devices.

2:30 PM CP04.00.05
Understanding Surface Degradation and Ligand Passivation-Assisted Stability of Hybrid Perovskites in Water Using Molecular Dynamics Simulations. Huanghun Zhou, Mingchao Wang, Jinfang Wang and Shangchao Lin; Materials Science and Engineering, Florida State University, Tallahassee, Florida, United States; Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, China; Mechanical Engineering, Florida State University, Tallahassee, Florida, United States; Materials Science and Engineering, Monash University, Melbourne, Victoria, Australia.

Organic-inorganic hybrid perovskites, such as the prototypical methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$, or MAPbI$_3$), have emerged as promising light absorbers in photovoltaic (PV) cells or as emitters in light-emitting diodes (LEDs). The strikingly high energy conversion efficiency up to ~20% enables hybrid perovskites as the key component of highly efficient solar cells. However, they generally suffer from moisture instability, which limits the long-term use of perovskite-based devices in ambient environment. In this work, in order to improve the surface moisture stability of MAPbI$_3$ in common humidity atmosphere, more specifically, to discover better ligands under a specific coverage on the [MAI]$^+$ surface to greatly improve the moisture stability and decrease the ion dissociation rate, we have applied molecular dynamics (MD) simulations and reaction kinetics theory to model the ion dissociation process and estimate the associated free energy barrier with and without ligand passivation. We have developed a new MD force field for MAPbI$_3$, which can match the density functional theory (DFT)-predicted elastic properties, experimental water contact angle on MAPbI$_3$, and DFT-predicted water infiltration and adhesion energies. We design MAPbI$_3$ with ligand-passivated surfaces by replacing MA$^+$ with ligands composed of long-chain alkyl-ammoniums. Ligands with different chain lengths, such as CH$_3$(CH$_2$)$_5$NH$_3$ ($n = 3, 5, 7$), and under different surface coverages ($\sigma = 25\%$, $50\%$, $75\%$, $100\%$), are considered here. We discover that ligand passivation can greatly help protect MA$^+$ on the surface due to the much higher dissociation free energy barriers of these ligands compared to that of MA$^+$. For iodine ions, ligand passivation can also shield them from water contacts, except for long-chain ligands, such as CH$_3$(CH$_2$)$_7$NH$_3$ ($n = 5, 7$) under full surface coverage ($\sigma = 100\%$), due to the reduced dissociation free energy barriers of long-chain ligands. As an interesting finding, the reduced dissociation free energy barriers for long-chain ligands under high surface coverages could be explained by their larger tendencies to micellize, which serves as additional driving force for their dissociation. This work significantly motivates future experimental efforts in designing new surface ligands to improve the moisture stability of hybrid perovskites.

2:45 PM CP04.00.06

We show how surfaces can be designed to redirect the momentum of the spreading lamella causing them to lift-off into 3-dimensional shapes thereby dramatically reducing the contact area. We design superhydrophobic surfaces with an in-plane discontinuity leading to the accumulation of vertical momentum resulting in the out-of-plane ejection of the lamella into water bowls. We demonstrate a two-fold reduction in the heat transfer between a cold rain and a warm surface. This novel approach can be broadly applied to other transport phenomena involving mass and energy exchange to limit heat loss under precipitation, icing of surfaces, reduce salt deposition on a surface exposed to ocean spray, or inhibit the formation of a water film on wings or wind turbine blades.

3:30 PM CP04.00.07
Defect Induced Surface Reactivity and Ion Transfer Process in TiO$_2$: Polymorphs Vijaykumar Munusugasan, Kee Sung Han, Venkateshkumar Prabhakaran, Yongsoon Shin, Tiffany Kaspar, Mal Soon Lee, Jaewon Lee, Vaithiyalingam Shuthananand and Suntharampillai Thevuthasan; Pacific Northwest National Laboratory, Richland, Washington, United States.

Reactivity and ion transfer processes across heterogeneous interfaces is the backbone of electrochemical devices such as batteries and dye sensitized solar cells. The complexity of reactivity and charge transfer across interfaces often arise from convoluted relations between surface chemistry (such as defect density, crystallographic orientation and functional groups) and exogenous drivers such as temperature and electric field. For example, technologically significant nanocrystalline TiO$_2$ with diverse surface chemistry renders a complex interfacial processes. To correlate the surface chemistry of TiO$_2$ with interfacial processes (reactivity and ion transfer), we performed a multimodal spectroscopic analysis in combination with ab-initio molecular dynamics (AIMD) calculations. The interfacial processes of anatase and rutile phase with varying surface chemistry against lithium bis(trifluoromethylsulfone)imide (Li-TFSI) salt were analyzed. We observed that, ubiquitous oxygen defects at TiO$_2$ surface regime enhance the molecular decomposition of TFSI anions. The thermally driven splitting of –CF$_3$ groups resulting in titanium oxyfluoride type bonding (O-Ti-F) at the near surface regime were observed in AIMD calculations and supported by multimodal spectroscopic measurements. The presence of free electrons due to fluoride ion transfer to TiO$_2$ anions. The thermally driven splitting of –CF$_3$ groups resulting in titanium oxyfluoride type bonding (O-Ti-F) at the near surface regime were observed in AIMD calculations and supported by multimodal spectroscopic measurements. The presence of free electrons due to fluoride ion transfer to TiO$_2$ anions. The thermally driven splitting of –CF$_3$ groups resulting in titanium oxyfluoride type bonding (O-Ti-F) at the near surface regime were observed in AIMD calculations and supported by multimodal spectroscopic measurements. The presence of free electrons due to fluoride ion transfer to TiO$_2$ anions. The thermally driven splitting of –CF$_3$ groups resulting in titanium oxyfluoride type bonding (O-Ti-F) at the near surface regime were observed in AIMD calculations and supported by multimodal spectroscopic measurements. The presence of free electrons due to fluoride ion transfer to TiO$_2$ anions.
Adhesion and interface formation are essential processes in friction, particle aggregation, and grain boundary formation. It is generally accepted that adhesion is anisotropic and the adhesion force depends on the mutual orientation of attracting interfaces. However, direct experimental measurement of the adhesion force and its orientation dependence has never been realized. Here, by combining in situ environmental transmission electron microscopy and atomic force microscopy, we directly measured the adhesion between two rutile TiO$_2$ (001) surfaces with controlled mutual orientation. The results show that the adhesion force is primarily van der Waals attraction between the two surfaces and is highest when the lattices of the two surfaces are aligned, demonstrating strong orientation-dependence. Moreover, the orientation dependence is not influenced by surface hydration; though, the adhesion force drops considerably with increasing water vapor pressure. Our work demonstrates a powerful method for quantitative study of nanoscale interface formation and strengthening, providing new insights to the driving force of orientated attachment of particles and friction anisotropy.

SESSION CP04.01: Interface Structure
Session Chairs: Fadi Abdeljawad and Eric Homer
Tuesday Morning, April 23, 2019
PCC West, 100 Level, Room 102 A

10:30 AM CP04.01.01
Connecting Atomic and Crystallographic Structure-Property Relationships of Grain Boundaries Eric R. Homer$^1$, Jonathan Priedeman$^1$, Conrad Rosenbrock$^1$, Oliver K. Johnson$^1$, Gus Hart$^1$ and Srikanth Patala$^2$; $^1$Brigham Young University, Provo, Utah, United States; $^2$North Carolina State University, Raleigh, North Carolina, United States.

Early grain boundary engineering work has demonstrated how significantly material properties can be improved with tailored microstructures. Unfortunately, continued improvement in this area will require complete structure-property relationships of grain boundaries, which are currently lacking. We describe tools and efforts to obtain both crystallographic structure-property relationships and atomic structure-property relationships. And since the two are must be combined to facilitate future design efforts, we detail efforts to find correlations between them. The properties of interest in this work are thermodynamic properties, like grain boundary energy, as well as kinetic properties, like grain boundary mobility.

11:00 AM CP04.01.02
Processing Routes for Controlling Disorder-Property Relationships in Metallic Alloys Daniel S. Gnanola$^1$, Glen Balbus$^1$, McLean Echlin$^1$, Charlotte Grigorian$^2$, Christoph Gammel$^3$, Daniel Kiener$^4$, Timothy J. Rupelt$^4$ and Tresa Pollock$^4$; $^1$Materials Department, University of California, Santa Barbara, Santa Barbara, California, United States; $^2$University of California, Irvine, Irvine, California, United States; $^3$Department Materials Physics, Montanuniversitat Leoben, Leoben, Austria.

The nonequilibrium nature of amorphous solids such as metallic glasses (MGs) shares intriguing commonalities with grain boundaries in nanocrystalline (NC) materials, owing largely to the multiplicity of energy states inherent to disorder. Here, we report on experimental studies of MG and NC materials and novel synthesis and processing routes for controlling the structural state—and as a consequence, the mechanical properties. Relaxation processes in disordered materials that facilitate atomic reconfigurations toward a lower energy state, such as low temperature annealing, have been shown to enhance mechanical strength while promoting shear localization. A particular focus in this talk will be on strategies for rejuvenation of disorder with the goal of suppressing shear localization and endowing damage tolerance. Parallels between our results and rejuvenation processes in glassy systems will be discussed in the context of controlling metastable structural configurations through novel processing routes.

11:30 AM CP04.01.03
Two-Dimensional Polymorphic $\{111\}/\{115\}$ Grain Boundaries in Si—Atomic Structure and Impurity Segregation Ability Yutaka Ohno$^1$, Hitoto Yoshida$^2$, Seiji Takeda$^2$, Tatsuya Yokoi$^1$, Atsuto Nakamura$^3$, Katsushi Matsunaga$^4$, Yasuo Shimizu$^5$, Naoki Ebisawa$^6$, Koji Inoue$^7$ and Yasuyoshi Nagai$^8$; $^1$IMR, Tohoku University, Sendai, Japan; $^2$ISIR, Osaka University, Osaka, Japan; $^3$GSE, Nagoya University, Nagoya, Japan; $^4$The Oarai Center, IMR, Tohoku University, Oarai, Japan.

Polymorphism in crystallography means the ability of a solid material to exist in more than one crystalline form, and the forms differ in physical and chemical properties even though their chemical components are identical. Recently, polymorphism in two-dimensional (2D) materials has been attracting interest in obtaining diverse properties that cannot be obtained in 3D forms [1, 2]. In this study, we have found 2D polymorphic nanostuctures self-organized inside silicon ingots grown by Czcrhalski (CZ)-method; they are composed of different 2D periodic units just along $\Sigma_9\{111\}/\{115\}$ grain boundaries (GBs) with a $\langle 110 \rangle$ tilt axis. The atomistic structure of the 2D polymorphic GBs, as well as their segregation ability, are determined by a 3D chemical nanoanalysis technique using atom probe tomography (APT) combined with scanning transmission electron microscopy (STEM) and ab-initio calculations [3].

STEM revealed that, $\Sigma_9\{111\}/\{115\}$ GBs have a periodic interface structure with a period of 2 nm along the GBs, and the GB unit is composed of $\Sigma_9\{221\}$-like and $\Sigma_9\{114\}$-like nanofacets involving 2 (110) reconstructed bonds (named type-I GBs in this paper) [4]. Ab initio calculations reveal the GB energy of 0.6 J/m$^2$, that is higher than the GB energy of $\Sigma_9\{221\}$ (0.18 J/m$^2$) and $\Sigma_9\{114\}$ (0.36 J/m$^2$) GBs. Also, the $\langle 110 \rangle$ bonds are rather longer in comparison with the $\langle 111 \rangle$ bonds in bulk Si. Thus, those long bonds would induce an energy in addition to the energy of $\Sigma_9\{221\}$-like and $\Sigma_9\{114\}$-like nanofacets.

The GB unit in type-I GBs is changed by annealing at 1100°C. The GB unit in the annealed GBs, that was observed in a cast-grown Si ingot [5], is composed of $\Sigma_3\{111\}$-like nanofacets involving 4 (110) bonds, with the period of 2 nm (type-II GBs). Type-II GBs can be introduced by forming stacking faults of low GB energy (~0 J/m$^2$) on the $\Sigma_9\{221\}$-like and $\Sigma_9\{114\}$-like nanofacets in type-I GBs. The GB energy of type-II GBs is estimated to be 0.45 J/m$^2$. Therefore, type-I GBs change into type-II GBs so as to remove $\Sigma_9\{221\}$-like and $\Sigma_9\{114\}$-like nanofacets of high GB energy, via the formation of $\Sigma_3\{111\}$-like nanofacets of low GB energy, even though 2 (110) bonds of high-energy are added in each GB unit.

APT reveals the oxygen segregation ability of type-I GBs (0.04-0.06 atoms/nm$^2$) and that of type-II GBs (0.03 atoms/nm$^2$). The ratio of the abilities is the same as the ratio of the GB energy of type-I and type-II GBs; i.e., the ability is proportional to the GB energy, as expected [3, 4]. We will discuss potential controls of the 2D polymorphic nanostuctures, as well as of their segregation ability, by changing the growth condition.


Acknowledgments: This work is supported by JST/CREST (Grant No. JPMJCR17J1, 2017-2023)

11:45 AM CP04.01.04

The scaling of behavior in ferroelectrics remains a topic of substantial interest given the need for device miniaturization and fundamental research. In recent years, a suite of reports has shown that the bulk piezoelectric functionality of thin ferroelectric films (approximately 30 nm or less) have a strong dependence on the surface chemical and structural state. Furthermore, these works suggest surface screening is a critical factor in understanding the bulk properties and switching behavior in thin film form, but precise mechanisms of this coupling are lacking. A key question that remains is the role of intrinsic as opposed to extrinsic screening on the properties of the thin ferroelectric films. In this work, we use BaTiO$_3$ (BTO) grown via pulsed laser deposition (PLD) as a model material system to explore the correlation between surface state and bulk properties. To carefully probe the
surface and bulk properties of BTO thin films, we use a combination of atomically resolved scanning tunneling microscopy (STM), non-contact atomic force microscopy (AFM), piezoresponse force microscopy (PFM), X-ray diffraction (XRD), and in-situ X-ray photoelectron spectroscopy (XPS). The aforementioned characterization techniques provide an experimental pathway to evaluate the correlation between the surface state and bulk piezoelectric properties.

SESSION CP04.02: Mechanically-Driven Transformations and Diffusion
Session Chairs: Eugen Rabkin and Jason Trelewicz
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 102 A

1:30 PM - CP04.02.01
Interface Diffusion-Controlled Pseudoelasticity of Metal Nanoparticles
Amit Sharma, Nimrod Gazit, Leonid Klinger and Eugen Rabkin; Department of Materials Science and Engineering, Technion-Israel Institute of Technology, Haifa, Israel.

An assembly of hemispherical Ag nanoparticles is prepared by solid-state dewetting of thin Ag film deposited on the sapphire substrate. The in-situ nanomechanical compression testing of the particles with a flat diamond punch inside the scanning electron microscope demonstrates the deformation behavior typical for the nucleation-controlled plasticity: high elastic deformation followed by an abrupt particles collapse. The latter is associated with the dislocations nucleation in otherwise pristine particle. The average contact pressure in the contact zone at the onset of dislocation-controlled plasticity is about 8 GPa, and does not depend on particle size. This observation supports the hypothesis that the pseudoelasticity of much smaller Ag nanoparticles observed by Sun et al. [Nat. Mater. 2014, 13, 1007] is intrinsically related to their ultrahigh strength. A stress-induced diffusion along the particle-substrate and particle-punch interfaces is identified as a factor controlling the pseudoelastic deformation. The corresponding diffusion model allows estimating the room-temperature self-diffusion coefficient of Ag along the Ag-W and Ag-Zirconia interfaces, which was quite close to the estimated value of the grain boundary self-diffusion coefficient in Ag. Based on this finding, the map of pseudoelastic deformation of several metals is proposed.

2:00 PM - CP04.02.02
Strain Relaxation in Low-Mismatched GaAs/GaAsBi$_{0.92}$Sb$_{0.08}$/GaAs(001) Heterostructures
Abhinandan Gangopadhyay, Aymeric Maros, Nikolai Falaleev and David J. Smith; Arizona State University, Tempe, Arizona, United States.

Semiconductor heterostructures enable band-gap engineering by combining two or more dissimilar materials, and are essential for many optoelectronic applications such as multi-junction solar cells, lasers and light-emitting diodes. However, differences in lattice parameters between film and substrate give rise to interfacial misfit strain. Misfit dislocations are introduced beyond a certain critical thickness, which will likely severely limit device performance by acting as sites for electron-hole pair recombination. Identifying the sources of these defects and understanding their evolution as a function of film thickness would possibly lead to identifying a path for minimizing defects in such heterostructures by optimizing growth conditions, film thickness, etc. In this study, the creation and evolution of structural defects in low-mismatched (misfit strain ~0.6%) GaAs (cap)/GaAs$_{0.92}$Sb$_{0.08}$/GaAs(001) heterostructures grown by molecular beam epitaxy have been investigated using transmission electron microscopy as well as high-resolution x-ray diffraction and atomic force microscopy (AFM). Three distinct stages of strain relaxation were identified in GaAs$_{0.92}$Sb$_{0.08}$/GaAs films with thicknesses in the range of 50-4000 nm, whereas 50-nm-thick GaAs capping layers exhibited only initial Stage-I relaxation. Aberration-corrected electron microscopy revealed that glide-set dissociated 60° dislocations were primarily formed during Stage-I relaxation. Lomer edge dislocations with complex core structure and curved dislocations prevalently with edge character formed in Stage-II and Stage-III of relaxation. Evolution of dislocation density at cap/film interfaces showed a strong correlation with the evolution of surface morphology at the growth front. Even though misfit strain was highest at the cap/film interface of the heterostructure with 4000-nm-thick film, dislocation density was lower in comparison with heterostructures with 1000-nm-thick and 2000-nm-thick films. AFM results indicated that smoothening of the growth front in the heterostructure with 4000-nm-thick film caused a decrease in the areal density of surface troughs which may act as preferred sites for heterogeneous nucleation of dislocation half-loops. Detailed consideration of different sources for threading dislocations and the experimental evidence of correlation between decreased dislocation density and decreased density of surface troughs led to the conclusion that heterogeneously nucleated surface half-loops are the major source of threading dislocations in these low-mismatched heterostructures [1].

Reference
[1] A. Gangopadhyay, A. Maros, N. Falaleev, D.J. Smith, Strain relaxation in low-mismatched GaAs/GaAs$_{0.92}$Bi$_{0.08}$/GaAs heterostructures, Acta Mater. 162 (2019) 103-115.

2:15 PM - CP04.02.03
Exploring the Impact of Strain and Droplet Formation on Phase Separation and Atomic Ordering in GaAsBi
Margaret A. Stevens, John McEleaney, Kevin Grossklaus and Thomas E. Vandervelde; Electrical and Computer Engineering, Tufts University, Medford, Massachusetts, United States.

III-V-Bismides are attractive materials for near- and mid-IR device applications due to their dramatic decrease in band gap with small incorporations of bismuth. The growth space is limited by the epitaxial mismatch. The resulting compressively strained films have exhibited a variety of phase separation characteristics, including lateral composition modulations [2], droplet induced composition inhomogeneity [3], and CuPt$_2$-type atomic ordering [4]. We have explored growing on InGaAs buffers layers as a method for reducing epitaxial compressive strain, suppressing surface droplet formation, and eliminating vertical phase separation through the bismide film layers.

GaAsBi epilayers were grown by solid-source molecular beam epitaxy on a Veeco GENXP10 MBE using a valved As$_2$ source and an effusion cell for bismuth. Samples were characterized by HRXRD to determine the average bismuth content and the strain state of the layers. AFM was used to analyze the droplet formation on the surface of the films. TEM and HAADF STEM were used to qualitatively characterize the bulk phase separation. By comparing samples grown on GaAs to samples grown on InGaAs buffers, we will draw connections between film strain, surface droplet formation, and phase separation. We are able to reduce the degree of phase separation that occurs in GaAsBi films, by growing on InGaAs buffers layers; thereby increasing film homogeneity and general suitability for optoelectronic applications.


2:30 PM - CP04.02.04
Dynamic Investigation of Titanium Disilicide Formation by In Situ TEM
Hsin Mei Lu, Chih-Yang Huang and Wen-Wei Wu; National Chiao Tung University, Hsinchu, Taiwan.

C54 titanium disilicide (TiS2) has attracted great attention in Fin Field-effect transistor (FinFET) application, since it has accompanied with promising advantages, such as low resistivity, outstanding reliability and low mobility in silicon substrate. In order to further investigating the structural properties, we observed the formation process of C54-TiS$_2$ by in-situ TEM in this study. During the heating process, Ti atoms diffused into Si$_{1-x}$Ge$_x$ substrate and nucleated afterward to form C54-TiS$_2$. It is remarkable that we also observed the occurrence of a novel type of texture-axiotaxy between C54-TiS$_2$ (110) plane and Si (001) plane at around 800 celcius degree. Axiotaxy is convinced to be produced from the epitaxial mismatch. The resulting compressively strained films have exhibited a variety of phase separation characteristics, including lateral composition modulations [2], droplet induced composition inhomogeneity [3], and CuPt$_2$-type atomic ordering [4]. We have explored growing on InGaAs buffers layers as a method for reducing epitaxial compressive strain, suppressing surface droplet formation, and eliminating vertical phase separation through the bismide film layers.


2:45 PM - CP04.02.05
Design and Control of Crystalline Phase Interfaces in Doubly-Epitaxial FeSe Thin Films
Sunzor B. Harris and Renato P. Camata; Physics, University of Alabama at
Grain Size Effects on Ni/Al Nanolaminate Combustion

For some material systems, one crystalline phase may exhibit growth of domains with different epitaxial relationships to the substrate or two phases may grow simultaneously with different orientations. This process, known as double epitaxy, creates thin film materials with many grain interfaces at fixed angles with respect to the substrate. This work demonstrates that double epitaxy in FeSe, an important superconducting compound with a complex phase diagram which is highly sensitive to stoichiometry. Conditions exist during pulsed laser deposition (PLD) that lead to the simultaneous epitaxial growth of the tetragonal (β-FeSe) and hexagonal FeSe (γ-FeSe) phases of FeSe in intermingled domains throughout the film, creating many phase boundary interfaces. We investigate the impact of PLD parameters on the double epitaxy of this interface-dominated material and identify the conditions under which double epitaxy is suppressed. The lattice parameters of β-FeSe and γ-FeSe are unsuitable for lattice-matching epitaxial growth on MgO. In the case of β-FeSe, the lattice parameter (a = 3.672-3.769 Å, depending on stoichiometry) differs from that of MgO (a = 4.211 Å) by more than the 9% normally tolerated for conventional epitaxy. The cubic structure of MgO, however, exhibits various domain matching epitaxial relationships with the various FeSe crystalline phases. This opens opportunities for engineering the internal interfacial boundaries of different FeSe phases by controlling the rotation of the epitaxial domains with processing parameters. A KrF excimer laser (1.4-3.4 J/cm²) was used to ablate a pressed, sintered target synthesized from FeSe powder. Targets were sintered in sealed quartz ampules at 700°C for 12 hours. Targets were ablated in high vacuum (10⁴ torr) with substrate temperatures in the 350-550°C range. FeSe films grown at temperatures between 350°C and 450°C with laser fluence fixed at 3 J/cm² showed the simultaneous epitaxial growth of both (001)-oriented β-FeSe and (101)-oriented γ-FeSe. The relative fraction of these two phases changes smoothly from majority β-FeSe at 350°C to majority γ-FeSe at 450°C. The β-FeSe phase grows aligned with the substrate and the γ-FeSe phase grows in two rotated domains, one dominant domain aligned with the substrate and a minor domain rotated by 45°. Atomic force microscopy (AFM) reveals the granular surface morphology with apparent grain sizes of 220-300 nm in films grown at 350°C and 450°C. The film grown at 400°C has a nearly equal fraction of each phase and the apparent grain size is found in the 120-200 nm range. The smaller grain size points to a larger number of phase interfaces, corresponding to an estimated number density of β-FeSe/γ-FeSe interfaces of 5.5x10⁹ cm⁻². Substrate temperature of 550°C results in a change in epitaxial orientation of β-FeSe from (001) to (101)-oriented. The (101) oriented β-FeSe grows in three domains, one aligned with the substrate and two others rotated by ±30°. AFM of the (101)-oriented FeSe shows large, micron scale grains leading to a much smaller grain interface number density than the biphasic films on the order of 10⁶ cm⁻². This growth technique shows the orders of magnitude scalability of in-plane interfaces of these epitaxially-oriented grains. At 550°C, reducing the laser fluence to 1.4 J/cm² increased the relative fraction of the γ-FeSe phase. The parameters of the PLD plasma plume are expected to influence the simultaneous epitaxial growth of the two phases by delivering a locally non-stoichiometric flux. Measurements of time and space resolved ion densities of the PLD plume will be presented and correlated with the emergence of γ-FeSe to determine the impact of the relative density of arriving ions on phase crystallization.

3:00 PM BREAK

SESSION CP04.03: Tailoring Properties by Controlling Interfacial Structure
Session Chairs: Martin Hamer and Jason Trelewicz
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 102 A

3:30 PM CP04.03.01
Grain Boundary Complexion Engineering—A Case Study of Silica and Rare-Earth Doped Boron Suboxide Armor Ceramics
Christopher J. Marvel1,2,3,4, Kieron F. D. Behler1,2,3,4, Jennifer Synowiezynski-Dunn1,2, Jerry C. LaSalvia1,2, Martin Hamer1,2,3,4
1Lehigh University, Bethlehem, Pennsylvania, United States; 2US Army Research Laboratory, Adelphi, Maryland, United States; 3SURVICE Engineering, Dumfries, Virginia, United States.

Grain boundary complexion engineering was recently introduced as a framework to be used to design grain boundaries and govern bulk material properties. The main conceptual tools of grain boundary complexion engineering are grain boundary complexion equilibrium diagrams and grain boundary complexion time-temperature-transformation (TTT) diagrams. Importantly, when the thermodynamic and kinetic diagrams are used in tandem, scientists and engineers have the ability to tailor classical processing conditions (e.g. chemistry, pressure, temperature, and time) to intelligently control grain boundary complexions, and specifically, complexion transitions from one complexion type to another. The ability to control complexion transitions is particularly important because a complexion transition could theoretically convert a tough material to a brittle material or an insulator to a conductor. The main objective of this talk will review the concepts of grain boundary complexion engineering and outline various approaches to develop the necessary complexion equilibrium and time-temperature-transformation diagrams. The second segment of this talk will summarize a grain boundary complexion engineering case study of silica and rare-earth oxide doped boron suboxide armor ceramics. Boron suboxide is being investigated as a promising armor ceramic because of its low density and high hardness, however, boron suboxide exhibits poor sinterability and fracture toughness. This case study outlines how grain boundary complexion engineering is used to control the thermodynamics and kinetics of grain boundary complexion transformations to improve sinterability and enhance fracture toughness. Boron suboxide powders were co-doped with silica and rare-earth oxide additives and the resultant microstructures were analyzed using advanced electron microscopy techniques to characterize grain boundary structures and quantify grain boundary segregation. The main observations include clear differences in microstructural evolution between the silica and rare-earth dopants, modified atomic structures with different excess grain boundary segregation concentrations, and improvements in bulk hardness.

4:00 PM CP04.03.02
Grain Size Effects on Ni/Al Nanolaminate Combustion
Brandon Witbeck1,2,3,4,5, and Douglas E. Spearot1,2,3,4,5
1Mechanical & Aerospace Engineering, University of Florida, Gainesville, Florida, United States; 2Munitions Directorate, Air Force Research Laboratory, Eglin AFB, Florida, United States.

Ni/Al reactive nanolaminates are systems of current scientific interest due to their highly customizable exothermic combustion characteristics. The high combustion temperatures normally tolerated for conventional epitaxy. The cubic structure of MgO, however, exhibits various domain matching epitaxial relationships with the various FeSe crystalline phases. This opens opportunities for engineering the internal interfacial boundaries of different FeSe phases by controlling the rotation of the epitaxial domains with processing parameters. A KrF excimer laser (1.4-3.4 J/cm²) was used to ablate a pressed, sintered target synthesized from FeSe powder. Targets were sintered in sealed quartz ampules at 700°C for 12 hours. Targets were ablated in high vacuum (10⁴ torr) with substrate temperatures in the 350-550°C range. FeSe films grown at temperatures between 350°C and 450°C with laser fluence fixed at 3 J/cm² showed the simultaneous epitaxial growth of both (001)-oriented β-FeSe and (101)-oriented γ-FeSe. The relative fraction of these two phases changes smoothly from majority β-FeSe at 350°C to majority γ-FeSe at 450°C. The β-FeSe phase grows aligned with the substrate and the γ-FeSe phase grows in two rotated domains, one dominant domain aligned with the substrate and a minor domain rotated by 45°. Atomic force microscopy (AFM) reveals the granular surface morphology with apparent grain sizes of 220-300 nm in films grown at 350°C and 450°C. The film grown at 400°C has a nearly equal fraction of each phase and the apparent grain size is found in the 120-200 nm range. The smaller grain size points to a larger number of phase interfaces, corresponding to an estimated number density of β-FeSe/γ-FeSe interfaces of 5.5x10⁹ cm⁻². Substrate temperature of 550°C results in a change in epitaxial orientation of β-FeSe from (001) to (101)-oriented. The (101) oriented β-FeSe grows in three domains, one aligned with the substrate and two others rotated by ±30°. AFM of the (101)-oriented FeSe shows large, micron scale grains leading to a much smaller grain interface number density than the biphasic films on the order of 10⁶ cm⁻². This growth technique shows the orders of magnitude scalability of in-plane interfaces of these epitaxially-oriented grains. At 550°C, reducing the laser fluence to 1.4 J/cm² increased the relative fraction of the γ-FeSe phase. The parameters of the PLD plasma plume are expected to influence the simultaneous epitaxial growth of the two phases by delivering a locally non-stoichiometric flux. Measurements of time and space resolved ion densities of the PLD plume will be presented and correlated with the emergence of γ-FeSe to determine the impact of the relative density of arriving ions on phase crystallization.

4:15 PM CP04.03.03
In Situ TEM Investigation of Low Resistivity NiSi Formation on Silicon Layer
An-Yuan Hsu, Che-H-Yang Huang, Kuo Lun Tai and Wen-Wei Wu; Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Nickel silicide (NiSi) thin films have various advantages for microelectronics processes, such as low resistivity and low formation temperature. Therefore, it has been widely used in semiconductor devices. The formation of NiSi thin film mainly depends on the mechanism of diffusion between Ni and Si. In order to understand its formation kinetics, in-situ transmission electron microscopy (TEM) is a powerful tool to study the diffusion behavior during the process. In this work, we successfully observed the process of diffusion by in-situ TEM. We chose silicon-germanium (SiₐGe₁₋ₐ) as strain layer to improve the electronic performance. During the heating process, Ni atoms would diffuse into SiₐGe₁₋ₐ layer at 400°C in the duration of 10 minutes heating. The HRTEM results and the corresponding FFT-DF demonstrated that the product was NiSi. In addition, we found that there is a specific orientation relationship of [120]NiSi//[01-1]HRT, and [002]NiSi//[1-1-1]HRT. Furthermore, the Energy Dispersive Spectrometer (EDS) analysis established the elemental composition for both as-grown and after-annealed samples, giving strong evidence for the formation of the NiSi. These results provide us useful information to grow low resistivity NiSi thin film.
Study on the Atomic Interaction of Si and Mn During the Eutectoid Transformation in High-Carbon Steel Linglehui Huang1, Yiyou Tu1, Xuefeng Zhou1 and Jianqing Jiang1; 1Southeast University, Nanjing, China; 2Nanjing Forestry University, Nanjing, China.

High-carbon steels (pearlitic steel) are widely used in the fields, including bridge cable, automobile tire cord and high-rise building, owing to the outstanding high strength and low cost. Micro-alloying is the common method to increase the strength of pearlite steels. In the simplest Fe-C-M (M: Mn, Si, Cr, Ni) ternary system, the effects of alloying elements have been extensively studied. For example, Mn, as the austenite stabilized element, delays the pearlitic transformation, improves the stability of cementite and retards the spheroidization of cementite lamellar; Si, as the non-carbide forming element, refines the lamellar structure of pearlite, increases tensile strength, improve softening resistance during tempering, and etc. However, in the complicated multicomponent system the partition and interactive effects among alloying elements needs to be attention, especially the interaction of alloying elements during the eutectoid transformation need to be further studied.

Therefore, in the present work the atomic interaction among Si, C and Mn in Fe-C-M-Si quaternary system during the eutectoid transformation is investigated using atom-probe tomography combining first-principle calculations. Two types of pearlite carbon steels with different Si contents are prepared. At the initial stage of eutectoid transformation, atom probe tomography observations indicate that Si is enriched at the ferrite side of ferrite-cementite interface, while Mn is enriched at the cementite side. This interfacial segregation phenomenon gradually diminishes or disappears as the transformation proceeds. Based on the results of first-principle calculations, Si moves from the core of cementite layer to the ferrite side of ferrite-cementite interface can obviously enhance the chemical bonding and stability of pearlite system. In the same manner, Mn atom moves from the core of ferrite layer to the ferrite-cementite interface, which improves the thermal stability of pearlite system. Therefore, Si/Mn segregates at each side of ferrite-cementite interface at the initial stage of pearlitic transformation. Furthermore, the partitioning ratio of Mn in high Si steel is higher than that in low Si steel, leading to more Mn partition into cementite. Based on the results of first-principles calculations, due to the strong repulsive force between Si and Mn at the interface of pearlite, the enrichment of Si in ferrite promotes the partitioning of Mn into cementite.

4:45 PM CP04.03.05 Interatomic Bonds and Elastic Properties of Σ5(210) Grain Boundaries in Ni3Si Compound Martin Zelený1, 2, Martin Frišek1, Monika Všínská3, 4, David Holeč4 and Mojmir Soběk1, 3, 51Institute of Physics of Charles University, Faculty of Mathematics and Physics, Charles University, Prague, Czechia; 2Institute of Materials Science and Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czechia; 3Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Brno, Czechia; 4Central European Institute of Technology, CEITEC MU, Masaryk University, Brno, Czechia; 5Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czechia, 6Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria.

We have performed an ab initio study of the elastic properties of the interface states in Ni3Si associated with the Σ5(210) grain boundary (GB). Ni3Si is well known structural material with a large potential for high temperature applications in corrosive atmospheres, which however suffers by low ductility with tendency to intergranular fracture. Rather complex tetragonal elasto-chemical aspects of the studied periodic GB approximants were found in the case of states with different atoms at the GB plane (either only Ni atoms (Σ5(210)(200)) or both Si and Ni atoms (Σ5(210)(200))). The Σ5(210)(200) GB state is predicted to have only a slightly lower interface energy of the two studied variants. The elastic constants are found to depend very sensitively on the GB plane chemical composition. In particular, the GB variant containing both Ni and Si atoms at the interface is shown to be unstable with respect to a shear deformation (one of the elastic constants, C66, is negative). This instability is occurs for a rectangular-parallellepiped supercell obtained when applying a standard coincidence-lattice construction. Our elastic constant analysis allowed us to identify a shear-deformation mode reducing the energy and eventually to obtain a mechanically stable ground-state characterized by a shear-deformed parallellepiped supercell. Nevertheless, a three-/eight-fold reduction of the elastic constant C66 when compared with the bulk value is identified as the crucial weakest link of the mechanical stability for the studied GB states. We have also partly stabilized this GB interface state by Al substituent replacing Si atoms at the GB.

Next, an origin of this elastic softening and instability of the rectangular-parallellepiped Σ5(210)(200) GB variant is discussed in terms of chemical inter-atomic interactions described by the crystal orbital Hamilton population (COHP). Lattice-dynamics properties represented by projected force-constant matrices on the unit vector along each bonding direction were considered as well. Such complex analysis reveals a weak interaction far from the GB interface between the Ni atoms in the 3rd plane and the Si atoms in the 5th plane. However, this bond weakening is a consequence of a very strong interaction between the Si atoms in the GB plane and Ni atoms in the 3rd plane off the GB interface. The same strong interaction was not observed when Si atom at the GB is replaced by Al. Thus the strong interaction near the GB plane makes this GB variant mechanically unstable.

Our study clearly shows the importance of anisotropic elastic-constant treatment as well as interatomic-interaction analysis for next studies of interface states close to GBs when determining origin of their mechanical (in-)stability. The sensitivity of elasto-chemical properties, which was additionally illustrated by studying the impact caused by Al atoms substituting Si atoms at the GB interface plane, paves a new way towards a solute-controlled design of GB-associated interface states with controlled tensorial elastic properties and stability.

CP04.04.01 Mesoscale Interface and Surface Characterization by μ-XRD Mapping on Mosaic and Lateral Grown Single Crystal Diamond Shengyun Bai1 and Elias Garratt; Chemical Engineering and Materials Science Department, Michigan State University, East Lansing, Michigan, United States.

For decades, diamond has shown superior properties that make it desirable for novel electronic materials. However, fabricating large size high quality single crystal diamond wafers faces multiple challenges. Lateral overgrowth and mosaic growth of CVD diamond make it highly possible for large size diamond wafers to be realized. Mesoscale characterization on the interface and surface of the grown CVD diamond is key to understanding how to eventually fabricate large size high quality single crystal diamond wafers.

In this work, mosaic and lateral single crystal diamonds were grown by Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD) on High Pressure High Temperature (HPHT) seeds and characterized by a micro x-ray diffraction (μ-XRD) mapping technique with a 300 μm slit to show the evolution of diamond crystal structure information during growth and provide feedback on growth strategies. By understanding how crystal structure evolves during growth we can understand the mechanisms linking processing conditions the structure and properties of grown material.

Our results demonstrate after growth and regrowth by MPACVD, variation in the structure and distributions of these variations evolves towards homogeneity. Measurements of the (400) phase for mosaic and lateral growth samples by high-resolution x-ray rocking curve (HRXRC) and 20-μ m-mapping technique. The overall misorientation of the merging CVD layers is shown to decrease with the regrowth from 0.225° (bottom layer plate) to 0.092° (uppermost layer plate). μ-HRXRC mapping results show a low mosaicity and μ- HR 2θ-a-scan shows a low average Full Width at Half Maximum (FWHM), 0.032° and high crystallinity. Typically lateral overgrowth shows a uniform misorientation at the growth front, ranging from 0.092° to 0.035°. In contrast, our mosaically joined samples show a non-uniform distribution in misorientation at the merging interface, displaying a biaxial deviation parallel and perpendicular to the interface. The preliminary data shows that after regrowth, this biaxial distribution tends toward uniformity, with regions of independent preferred orientation overtaken by a single, new orientation. We will discuss this phenomenon in terms of step-flow overgrowth and energetically favorable states of the diamond crystalline phase during epitaxial lateral overgrowth in the extreme plasma environment.

CP04.04.02 Analytical Diffuse Layer Models in Electronic Structure Simulations Matthew Truscott and Oliviero Andreussi; University of North Texas, Denton, Texas, United States.

Continuum models will be critical towards the computational characterization of the diffuse layer at electrochemical interfaces. Recently, a number of different approaches have been proposed. Here we will present a new class of methods based on a planar averaged approximation and the Gouy-Chapman theory for electrochemical interfaces. These models potentially constitute a powerful set of tools for investigating one-dimensional surfaces, with several advantages over their more generalized counterparts. They exploit the
analytic solution for the one-dimensional complex electrostatic problem, are computationally inexpensive, and are not affected by any imposed periodicity. Charged metal solvent interfaces and their experimentally recorded differential capacitance values present a benchmark to compare candidate models. We will present the theory, implementation, testing, and applications.


CP04.04.03
Computational Investigations of Surface Adsorption of Ethane on M1 Catalyst (Mo-V-Nb-Te-O) Byryton H. Anderson, Matthew L. Jones and Eric Jankowski; Boise State University, Boise, Idaho, United States.

Ethylene is a high-value chemical that is an essential building block for polymers and other designer molecules. Producing ethylene from ethane (a more plentiful feedstock) is, therefore, a high-value activity, but one that requires a lot of energy. The use of catalysts to more efficiently perform chemical reactions, for example by lowering energy barriers for reaction pathways, therefore has the potential to save billions of dollars annually at production scales. The oxide Mo-V-Nb-Te-O (M1) is one such catalyst, but one whose efficacy degrades at elevated temperatures. In this work, we aim to understand the dynamics of ethylene on the surface of M1 to inform strategies for improving M1’s efficacy or lower its optimal operating temperature. Specifically, we develop tools that facilitate molecular modeling of organic molecules including ethane and ethylene on M1 surfaces and use them to study surface dynamics. We implement a combination of the OPLS-aa and UFF force fields and measure surface residence times of ethylene and ethane as a function of temperature. These measurements show ethane preferentially adsorb near Vanadium and Tellurium sites, informing strategies for increasing adsorption selectivity towards Vanadium. We investigate candidates for surface patterning and discuss anticipated changes in catalyst effectiveness.

CP04.04.04
Surface Characteristics of Accident Tolerant Fuel Cladding and their Potential Impact in Critical Heat Flux Rajañita Umreyati1, Daniel Ginestro2, Jessika Rojas3, Sama Bilbao1, Mark Anderson1, Barret Elward1 and Raul Reback2; 1University of Wisconsin-Madison, Madison, Wisconsin, United States; 2General Electric, Boston, Massachusetts, United States; 3Virginia Commonwealth University, Richmond, Virginia, United States.

Enhanced Accident Tolerant Fuels (ATFs) are defined as nuclear fuels that can tolerate a severe loss of active cooling in the reactor core for a considerably longer period of time than the current UO2 – zirconium alloy fuel system, while maintaining, or preferably improving, the fuel performance during normal operations and operational transients. The Critical Heat Flux (CHF) is one of the key parameters used to evaluate the thermal performance of a fuel product and to establish safety and operational margins. Preliminary studies for the proposed ATF concepts indicate that their cladding surface characteristics may result in substantial impacts in their CHF behavior. This work aims to investigate the surface characteristics of ATF cladding tubes of C26M, and APMT (both FeCrAl alloys) manufactured using industrial procedures. A comparison of their surface characteristics with current fuel cladding of Zircaloy-2 and Zircaloy-4 will be presented. Various roughness parameter, contact angle, and oxide layer thickness will be assessed using advanced materials examination techniques such as Profilometry, Atomic Force Microscopy, Contact Angle Goniometry and Scanning Electron Microscopy. Recent research has evidenced that surface roughness and contact angle may play an important role in the CHF enhancement. Further work will be focused on conducting a series of CHF experiments, at low and high pressure, with advanced temperature and fluid measurement instrumentation to obtain high fidelity qualitative and quantitative measurements of the thermal-hydraulic behavior of the ATF cladding under evaluation.

CP04.04.05
Perovskite Alloys and Metal Halides at the Interface—Crystallographic Orientation and Environmental Degradation Timothy Slepner, Daniel Houck, Yangning Zhang, Mokshin Suri and Brian A. Korgel; McKetta Department of Chemical Engineering and Texas Materials Institute, University of Texas-Austin, Austin, Texas, United States.

Hybrid organic-inorganic perovskites (HOIPs) such as methylammonium lead iodide (MAPI) and methylammonium lead bromide (MAPBr) have attracted much attention as solution-processed semiconductors that could be used in high performance optoelectronic devices such as photovoltaics, light emitting diodes, lasers, and X-ray detectors. These materials exhibit long carrier diffusion lengths, large absorption coefficients, and high photoluminescence quantum yields. For commercial applications, however, HOIPs suffer from significant humidity-induced degradation. Here, we report the stabilizing and destabilizing effect of B-site substitutional doping in HOIP materials, and discuss how surface doping at the B-site can induce preferential crystal orientation.

Substitutional doping of MAPI with Bi was found to lead to a stabilizing effect at high humidity, but a destabilizing effect at lower humidity. With 5 mol% Bi in MAPI, UV-Vis-NIR absorbance spectroscopy and X-ray diffraction (XRD) showed that at 90% relative humidity, the films took 72 h to fully degrade compared to 24 h for the undoped MAPI films. At the lower humidity of 60% RH, the undoped MAPI films were more stable than the Bi-doped MAPI films. The MAPI films were stable for 14 days; whereas, the Bi-doped MAPI films degraded after only 10 days.

While MAPI is a promising photovoltaic material, certain tandem cell and LED applications require wider band gap HOIPs, such as MAPBr. However, the random orientation of grains in MAPBr thin films made from commonly employed synthetic methods may hinder these devices’ effectiveness. Here we report the incorporation of Ag into MAPBr films induces a preferential (100) crystallographic orientation on any substrate and increases crystal grain size of thin film cubic MAPBr. X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), and time-of-flight second ion mass spectrometry (TOF-SIMS) revealed that Ag accumulates at the interfaces of the MAPBr film, which appears to be the reason for the preferred orientation of the film on the substrate. Elemental maps and grazing incidence wide angle X-ray scattering (GIWAXS) of the Ag-doped films also showed the emergence of secondary methylammonium silver bromide phases. These regions in the film could create recombination centers in photovoltaic devices (PVs). PVs were fabricated with MAPBr and Ag-doped MAPBr films. Despite the differences in crystallographic orientation and crystal grain size, there were no observed differences in the performance of these perovskite PVs up to 2 mol% Ag incorporation, at which point PV performance became worse with increasing silver content.

CP04.04.06
Membrane Characterization Through Electrocompression Joyce E. Bevrouthy and Eric Freeman; College of Engineering, The University of Georgia, Athens, Georgia, United States.

Chloroethers is an amphiphilic molecule present in cellular membranes at different concentrations depending on the cell’s role and functionality. It is uniquely structured as its hydrophilic head is much smaller than its bulky hydrophobic tail. When present in a phospholipid leaflet cholesterol behaves according to the umbrella model, filling the gaps in between phospholipid molecules and reducing the area per lipid. This provides an ordering and condensing effect for the membrane. The effect of cholesterol on cell membranes has been investigated and it has been seen to minimize its permeability and move the membrane from a liquid disordered to a liquid ordered state. These mechanics may be measured through the measurement of the interfacial tensions of lipid monolayers and bilayers with and without cholesterol.

In this work, the droplet interface bilayer (DIB) technique is used to investigate cholesterol’s effect on surface tension and the membrane structure. Based on lipid-coated aqueous droplets adhering in an oil medium, the DIB method enables linking droplet mechanics and membrane mechanics for interpreting changes in the membrane structure through droplet-droplet adhesion and the angles of contact at the droplet intersections. It is a purely fluidic method where the droplets are minimally constrained and the membrane is free to expand on the interfacial tensions. By observing the changes in the droplets’ adherence while measuring the membrane properties through electrophysiology, one can calculate membrane’s tension, specific capacitance, applied stress and resulting strain.

Pendent drop tensiometry was used to investigate the changes in the monolayer surface tension with increasing amount of cholesterol. Higher monolayer tensions were observed with increasing cholesterol concentrations, along with increasing bilayer tension and adhesion energy. Next, membrane properties with varying cholesterol were measured. The membranes exhibited a non-linear reduction in thickness with the increasing cholesterol mole fractions. To understand cholesterol’s impact on membrane’s structure and rigidity, an electric field was gradually increased across the membrane until failure providing membrane compression beyond the equilibrium dimensions. The membrane thickness along the corresponding electrical stress were measured for each voltage. Plotting the pressure versus membrane thickness for different cholesterol concentrations shows that cholesterol does not affect the critical stress at failure. However, it significantly reduces membrane thinning. Adding at 30% cholesterol reduces membrane thinning by more than half. This indicated that cholesterol enhances the stiffness of the membrane, making it more rigid and resistant to transverse compression.

CP04.04.07
Generation of Shape-Tuned, Monodisperse Block Copolymer Particles Through Particle Restructuring by Solvent Engineering Jae Man Shin, Young Jun Lee, Mingoo Kim, Kang Hee Ku, Junhyuk Lee, Yongjo Kim, Hongseok Yun and Bumjoon Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).
Controllability of the shape, size, and internal structure of block copolymer (BCP) particles as well as their uniformity is crucial to determine their utility and functionality in the practical applications. Here, we demonstrate the particle restructuring by solvent engineering (PRSE) strategy that combines membrane emulsification and solvent annealing processes, to produce monodisperse particles using functional BCPs with controlled size, shape, and inner structure. Importantly, the advantage of our PRSE approach is the general applicability to various types of functional BCPs including polystyrene-block-polystyrene (PS-b-PS), polystyrene-block-polystyrene (PS-b-PDMS), and polystyrene-block-polystyrene (PS-b-PDVP). PRSE starts with producing monodisperse BCP spheres in a wide range of particle size (from hundreds of nanometers to tens of several microns) using membrane emulsification, followed by successful transformation to shape-anisotropic BCP particles by solvent annealing under neutral wetting condition. Monodispersity of particle size was maintained during the PRSE, and the shape transformations to both prolate and oblate shaped ellipsoids were successfully achieved. Our approach was effective in controlling the aspect ratio (AR) of particles over wide ranges, from 1.0 - 2.5 and 1.0 - 5.0 for prolate and oblate ellipsoids, respectively. Also, observed AR of the particles was well-supported by theoretical calculation based on the model describing the particle elongation. Further investigation on the shape transformation kinetics during the PRSE revealed that the morphology transformation was driven by reorientation of BCP microdomains, whose kinetics was strongly associated with the overall molecular weight of BCP and the annealing time.

Surface Energy Measurements by Three Liquid Contact Angle Analysis Correlated with Ion Beam Analysis of Thin Silicon Oxides as a Function of Dopant Species and Concentration Saakeh R. Narayan 1,2, Jack M. Day 1, 2, 3, Nikhil Suresh 1, 2, 3, Nicole Herbots 1, 2, 3, and Robert J. Culbertson 1, 2, 3 1Department of Physics, Arizona State University, Tempe, Arizona, United States; 2SiO2 Innovates, LLC, Tempe, Arizona, United States; 3AccuAngle Analytics, LLC, Tempe, Arizona, United States; 4MicroDrop Diagnostics, LLC, Phoenix, Arizona, United States.

Surface energy and hydro-affinity play a significant role in device manufacturing and semiconductor processing. Surface reactivity, bonding and passivation is as critical as structure and composition for gate oxides, ohmic contact formation, heterostructures, opto-electronic and piezo-electronic device integration.

In this work, the effect of doping species upon Si(100) total surface energy, \( \gamma_s \), hydro-affinity, and reactivity, is investigated for three n-type dopants, phosphorus, arsenic or antimony, and two p-type dopants, boron or gallium, [2] by new quantitative measurements via Three Liquid Contact Angle Analysis (3LCAA)[1] correlated with Ion Beam Analysis (IBA), as a function of concentration.

3LCAA and the van Oss-Chaudhury-Good (vOOG) theory yield \( \gamma_s \) from three interactions, the Lifshitz-van der Waals interaction energy \( \gamma_W \), the interaction energy with electron donors \( \gamma_\alpha \), and acceptors \( \gamma_\beta \), measured via the contact angles of three liquids.

A new automated image analysis algorithm, DROP™, [3], yields contact angles within \( \pm 1\% \) and \( \pm 3\% \) in minutes. DROP™’s accuracy makes possible quantitative analysis of \( \gamma_s, \gamma_W, \gamma_\alpha, \gamma_\beta \), and \( \gamma_r \) as a function of doping species and concentrations.

Ion Beam Analysis (IBA) can detect oxygen coverage and elemental composition. High resolution IBA combines \( \phi \)O16, O16\( ^{3.039\pm0.01 \text{ MeV}} \) nuclear resonance with \( \sim 111\) channeling detects oxygen within 5%, or about 6x10^16 at/cm^2. Rutherford Backscattering Spectrometry (RBS) combined with <111> channeling can detect dopants with a sensitivity that increases quadratically with their atomic number, thus \(-4x10^{15}\) boron/cm^2, or 1 at.%; \(-4x10^{15}\) phosphorus/cm^2, or 0.1 at.%; \(-1x10^{15}\) gallium/cm^2, or 0.02 at.%; \(-1x10^{15}\) arsenic/cm^2, or 0.02 at.%; \(-4x10^{16}\) antimony/cm^2, or 0.01 at.% [2]. Oxygen coverage measured by IBA, along with doping levels and dopant species, can be correlated with \( \gamma_s, \gamma_W, \gamma_\alpha \), and \( \gamma_r \) measured by 3LCAA on both as-implanted and Rapid Thermal Annealed (RTA) Si(100). Si(100) amorphizes with increasing ion dose and defect concentrations, which catalyzes native oxide formation. During RTA, Si(100) recrystallizes and incorporates dopants into substitutional lattice sites. However, native oxide formation and dopant segregation modify final native oxide composition and thickness, as well as total surface energy and the surface interactions with donors and acceptors.

Higher dopant concentrations in both p-type and n-type doped Si(100) result in larger oxygen coverage and thus thicker native oxides, as measured by IBA, and lower surface energies as measured by 3LCAA. As expected, resulting surfaces are more hydrophobic and less reactive than as-implanted Si(100).

3LCAA also finds that as Si resistivity increases, \( \gamma_s \) also increases, showing that lower doping concentrations result in a more hydrophilic and more reactive surface [3]. Implanted Si is then etched, which removes surface oxides, and recrystallized by RTA to electrically activate dopants, regrowing a new native oxide. Longer RTA processes cause thicker oxides to form, along with higher segregation of n-type dopants at the Si-SiO\(_2\) interface. Hence, electrically activated n-type dopants enhance oxidation. The opposite effect is observed for recrystallized p-type doped Si, which shows thinner native oxides than as-implanted Si. 3LCAA, combined with IBA, can accurately measure changes to native oxide surface energies, hydro-affinity and reactivity as a function of dopant species and dopant concentration. These insights from 3LCAA expand understanding of dopants’ influence upon native oxide formation and of surface engineering for heterostructure formation by heteroepitaxy, conventional wafer bonding and NanoBonding™ [3].


Fabrication of High-Pressure-Phase \( \alpha \)-PhOx-Type TiO\(_2\) Epitaxial Thin Films via Ultrahigh Pressure Treatment Yuki Sasaki 1, Hiroaki Asoma 1, Koki Kanatani 1, Kazunori Nishio 2, Ryota Shimizu 2, Norimasa Nishiyama 1, 3 and Taro Hitosugi 1, 3 1School of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, Japan; 2PRESTO, Japan Science and Technology Agency, Saitama, Japan; 3Laboratory for Materials and Structures, Tokyo Institute of Technology, Kanagawa, Japan.

Ultrahigh-pressure (HP) polymorphs such as diamond exhibit unique physical properties. There are many HP polymorphs that can be recovered to the ambient pressure to be utilized in industry. However, some of the HP polymorphs that are thermodynamically stable under HP (> 10 GPa) transforms into amorphous structure or different crystalline phases during decompression. If this back-transformation can be suppressed, we can obtain some useful HP polymorphs to be utilized in future. As a possible solution, we combined the epitaxial thin film growth technique with HP synthesis method using a multi-anvil apparatus.

We first investigated a HP-phase, \( \alpha \)-PhOx-type titanium dioxide (\( \alpha \)-TiO\(_2\), orthorhombic, \( a = 0.454 \text{ nm}, b = 0.549 \text{ nm}, c = 0.491 \text{ nm} \)). Unfortunately, most of the reported data was about the product in form of powder, and only a few reports about the fabrication of single crystals are currently available. In particular, single-phase \( \alpha \)-TiO\(_2\), epitaxial thin films has not been reported. In this study, we report the fabrication of the high-quality single-phase \( \alpha \)-TiO\(_2\)(100) epitaxial thin films.

Thin films of epitaxial rutile TiO\(_2\)(100) (thickness: ~100 nm) were deposited as precursors on Al\(_2\)O\(_3\)(001) (5 mm in diameter and 0.5 mm in height) using pulsed laser deposition. HP treatment for thin films was performed using a Kawai-type multi-high-pressure apparatus. The precursor thin film was heated up to 1000°C under HP of 8 GPa, and then kept for 0.5 h. After the heating step, cooling was started down to room temperature (RT), followed by decompression.

As a result, a successful single-phase \( \alpha \)-TiO\(_2\)(100) epitaxial thin film has been obtained. It should be stressed here that rocking-curve full width at half maximum of the 20 peak showed a quite small value of 0.113°, indicating very high crystallinity. Our present study indicates that HP treatment to thin film samples allows us to fabricate high-quality HP-phase epitaxial thin films.

Transverse Printing of Colloidal Crystals Based on UVO Mediated Polymer Degradation Rabhrata Mukherjee 1, 2, 3 1Indian Institute of Technology Kharagpur, Kharagpur, India.

It is well-known that mono-dispersed colloidal particles self-assemble into hexagonal close-packed (HCP) structures, under appropriate conditions, which are also known as two-dimensional (2D) colloidal crystals. While various techniques, such as sedimentation, confined convective self-assembly, dip coating, drop casting, evaporative drying, electrophoretic deposition, self-assembly at the gas-liquid interface and Langmuir–Blodgett (LB) technique, inkjet printing etc. has been used for making such arrays, spin coating has its own advantage due to direct compatibility with microelectronic processing, pattern uniformity and requirement of very small amount of colloidal dispersion. We first show...
that monolayer colloidal crystal formation by spin coating is possible only in a narrow parametric window involving spin speed, substrate wettability, particle size, and substrate pattern geometry, in a case a topographically patterned substrate is used for template guided assembly. Subsequently, I will highlight a facile colloidal transfer printing method that relies on UVO mediated degradation of a sacrificial PMMA thin film. The method is capable of transferring both hexagonal closed packed (HCP) and template guided non-HCP arrays of inorganic or polymeric colloids onto any hydrophobic or hydrophilic target surface, which can be smooth, rough, or even curved. The method does not require any surface modification of the target substrate or any medium to facilitate the transfer. Finally, I will show that in certain cases the transferred particle array can significantly enhance the anti-reflection property of the target surface and can also be used as a template for growing patterned Zinc Oxide Nano Rod array which exhibit Self Cleaning property.

Key References:
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M. Banik, N. Bhandaru and R. Mukherjee, Chem Comm. 54, 3484, 2018

CP04.04.11

Nanostructured carbons are common components of electrodes used for energy-storage and -conversion applications to impart enhanced electronic conductivity that sustains high-rate operation, to support dispersed active materials (e.g., electrocatalytic metals and oxides), and to contribute to the physical structure and integrity of the electrode. Often overlooked in the design and characterization of such electrode structures is the critical nature of electronic/chemical/physical interactions at the junction of carbon with the nanoscale phases that impart desired storage or electrocatalytic functionality. Our own experience with such multifunctional compositions shows that we still “leave on the table” too much energy and power performance as a consequence of sub-optimal interfacial design. In order to explore these fundamental questions, we step back from the complexity of 3D electrode architectures to planar electrode configurations that otherwise mimic the material characteristics of practical electrode structures. Carbon films deposited onto planar substrates by vapor-phase pyrolysis of benzene and related monomers serve as model interfaces that we then modify with charge-storing metal oxides, electroactive polymers, and metal colloids [1]. The resulting 2D interfaces are characterized by classical electroanalytical methods to determine fundamental properties such as electron-transfer rate constants and impedance-driven response times. These substrates are also amenable to interrogation by scanning probe microscopy, including in-situ monitoring of conductivity and surface morphology under potential/current control. Lessons learned from these model 2D interfaces are readily applied to the redesign of practical 3D electrode structures in next-generation electrochemical capacitors and batteries.


CP04.04.12

Myriads of electrode materials with interesting nanostructures have been fabricated for a range of electrochemical applications. Beyond the increases in their surface area, unconventional properties have been observed along with the development of new approach and methodologies to analyze and utilize such properties. For instance, once a redox-active molecule diffuses into the nanoscale cavity of the electrode, it frequently collides with the inner electrode surface before it escapes the cavity, which is termed nano-confinement effect. This effect can specifically amplify the signals of slow electron transfer reactions (e.g., glucose oxidation) and has been established as a new mechanism for sensing the target materials that have slow electron transfer kinetics.

In this study, we fabricated a Au nanopillar electrode and devised a new electrochemical platform using redox cycling reaction to utilize the nano-confinement effect of the Au nanopillar electrode, which is applicable even to the fast electron transfer reactions as demonstrated by facilitating the electrochemical reaction of a specific biomarker (i.e., pyocyanin which has fast electron transfer kinetics) of bacterial infection (i.e., Pseudomonas aeruginosa). The Au nanopillar electrode was fabricated by first treating a polymer substrate with plasma to render an array of polymer nanopillars on the substrate and then depositing Au onto the plasma-treated substrate to the appropriate thickness to form nanoscale inter-pillar space. The Au nanopillar surface was modified with the redox cycling counterpart of pyocyanin so that the pyocyanin confined in the inter-pillar space underwent repetitive cycles of reduction (by the electrode) and oxidation (by the redox cycling counterpart tethered to electrode surface) reactions resulting in the amplification of the pyocyanin signal. This redox cycling-assisted signal amplification was clearly observed with the Au nanopillar electrode with higher amplification by taller Au nanopillars while the amplification was insignificant for the flat Au electrode, demonstrating the nano-confinement effect of Au nanopillar electrodes. As a result, the sensitivity in measuring pyocyanin was improved by the Au nanopillar electrode compared with the flat Au electrode. We believe that this new platform based on the surface-bound redox cycling reaction could overcome the limit in applicability of the nano-confinement effect.

CP04.04.13
Ordering and Miniaturization in Dewetting of Pre-Patterned Thin Polymer Films and Bilayers with Patterned Interface Nandini Bhandaru; Birla Institute of Technology and Science Pilani, Hyderabad Campus, Hyderabad, India.

Liquid thin films generate intriguing flow regimes and under specific conditions, lead to disintegration and de-wetting with the formation structures of submicron feature size. This concept has been well utilized as a non-lithographic route for creating meso-scale structures, where the structures can be ordered by guiding the instability pathway using a template. We show that patterns present on the surface of a polymer thin film (polystyrene) on a flat substrate can result in an ordered dewetted morphology under certain conditions. The pre-patterned polymer thin film undergoes pattern directed rupture along the thinnest parts of the film when the initial local thickness over these zones ($h_{in}$) is reduced to a limiting thickness ($h_{nm} = 10$ nm). In addition, depending on the periodicity of the imprinted patterns, the wavelength of instability corresponding to $h_{nm}$ must be lower than the width of the patterned grooves ($h_{l}$). A morphology phase diagram is constructed which indicates a transition from the surface tension induced flattening to the ordered pattern directed rupture. The versatility of this technique is in its ability to form myriad of aligned meso-patterns starting from a simple grating structure on the film surface. We further extend this concept to polystyrene-poly(methylmethacrylate) bilayers with a patterned polymer-polymer interface, where the instability is more complex due to coupled deformation of multiple, confined interfaces. This leads to creation of exotic patterns such as submerged, embedded and core shell structures, which are beyond the capability of standard lithography methods. The morphology of the evolving patterns is controlled by several parameters including the initial film thickness ($h_{i}$), pre-pattern amplitude ($h_{p}$), duration of solvent vapor exposure and wettability of the stamp used for pre-patterning the film. The evolution can be interrupted at any intermediate stage thereby achieving patterns on demand, which are well ordered as well as significantly miniaturized as compared to features obtained from dewetting of a flat film of same initial thickness.

References

CP04.04.14
Analysis of Deep Level and Oxide Interface Defects Using 100V HF Schottky Diodes and MOS CV’s for Silicon and 4H SiC HV MOSFE Ts, Advanced Power Electronics and RF ASIC James Pan; ATL, Northrop Grumman Electronic Systems, USA, Maryland, United States.

In this paper we report high voltage MOS and Schottky Diode CV techniques for silicon and SiC power devices. 4H Silicon carbide is a wide bandgap semiconductor suitable for high voltage power electronics and RF applications due to high avalanche breakdown critical electric field, and thermal conductivity. The performance of various power devices, which may include MOSFET and Static Induction Transistor (SIT), can be affected by the deep level traps in the substrate and the oxide interfacial defects. We have characterized deep level trap (High Voltage Schottky Diode HF CV) and oxide interface trap densities (High Voltage HF MOS CV), measured the device channel doping profile for both 4H SiC and silicon, gate metal workfunction, and simulated the effects on DC/AC performance.

TCAD simulation is done for a high voltage RF SIT. Pinch voltage ($V_{Pinc}$, as defined by the gate voltage required to turn the device off for a certain applied drain voltage) may be affected by the interface charges. Generally speaking, the $V_{Pinc}$ is very sensitive to the channel doping concentration.
Tensile Deformation Behavior and Inelastic Strain Recovery in Cu/Co Nanolaminates
Rohit Berlia and Jagannathan Rajagopalan; Arizona State University, Tempe, Arizona, United States.

The deformation behavior of nanostructured metallic multilayers has been extensively investigated because of their superior mechanical properties, primarily via nanoindentation and micropillar compression experiments. Here, we report tensile measurements on a Cu/Co nanolaminate with 4 nm layer spacing. The nanolaminates exhibit a flow strength as high as 2 GPa and failure strains of 3-4%. Interestingly, significant inelastic strain recovery was observed both during and after unloading, with further recovery occurring upon heating. In addition, the stress-strain slope during the initial stages of unloading was considerably higher than the expected elastic modulus, suggesting the presence of a super modulus effect due to the large coherency strain.

Tunable Surface Area and Electrochemical Capacitance of MnO3 Nanofibers Through Controlled Calcination
Molly Brockway and Jack L. Skinner; Mechanical Engineering, Montana Technological University, Butte, Montana, United States.

Electric double layer capacitors, or supercapacitors, have high theoretical capacities and faster charge/discharge rates than Li-ion batteries. Because they store charge via electrostatic interactions between the electroactive surface and ions in the electrolyte, increased specific surface area of electroactive material will increase the theoretical storage capacity of next-generation devices. Nanofiber-based electrodes have fewer issues with agglomeration and better long-term stability than nanoparticle-based electrodes, while maintaining extremely high surface area to volume ratios. As a potential electrode material, MnO3 is low-cost, naturally abundant, and environmentally benign. Electrospinning with subsequent thermal decomposition is a facile fabrication method for creating MnO3 nanofibers. Composite fibers consisting of a coordination polymer, polyvinylpyrrolidone, and oxide precursor, manganese acetate tetrahydrate, are electrospun. Calcination is used to burn out the polymer matrix and convert the salt to manganese oxide while retaining
The high aspect ratio fiber morphology.

Although Mn$_2$O$_3$ nanofibers have been prepared by thermal decomposition of a coordinating polymer-oxide precursor composite fiber, the influence of calcination conditions on specific surface area have not been well-explored. The proposed work will examine the effects of calcination time, temperature, and environmental composition on fiber surface area and corresponding electrochemical capacitance as compared to nanoparticle-based electrodes. Thermal analysis will be performed with thermogravimetry and differential scanning calorimetry to determine glass transition and decomposition temperatures of the as-spun composite fibers. The post-calcination fibers will be examined with X-ray diffraction to confirm phase and obtain information on crystallite size. Scanning electron microscopy will be used for morphological examination and qualitative examination of porosity resulting from changes in calcination parameters. To quantify changes in specific surface area, the Brunauer-Emmett-Teller (BET) method will be used on calcined fibers and compared to values measured for nanoparticles prepared from the oxide precursor. Increased surface area detected by BET may not necessarily be accessible to ions in the electrolyte, so to evaluate the accessible surface area, the fibers and particles will be processed into working electrodes. Electrochemical analysis including cyclic voltammetry and linear voltammetry will be utilized to assess the accessible surface area of fiber-based vs. particle-based electrodes based on measured capacitance. Preliminary results have shown that modifications to the gas composition and calcination time result in varied porosity, surface features, and cross-sectional morphologies. An understanding of the relationship between processing conditions and fiber morphology will allow for tunability of enhanced surface area, electrochemical capacitance, and supercapacitor performance.

CP04.04.18
Passivation and Positive Band-Edge Shift of Monocrystalline $p$-Silicon Through Surface Chemical Functionalization with Mixed Monolayers Miguel Caban-Acevedo, Bruce S. Brunsvichg and Nathan S. Lewis; Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States.

Controlling charge equilibration and recombination at semiconductor interfaces is essential for the design of efficient and cost-effective silicon-based devices in applications such as photovoltaic solar cells, microelectronics, and sensors. Towards the exploration of new pathways to manipulate the electronic properties of semiconductor interfaces, in this work we report our ongoing investigation into the utilization of surface chemical functionalization as a strategy to passivate the interfacial recombination and tune the energetic alignment of silicon surfaces. Our research efforts focus specifically on the covalent functionalization of $p$-type silicon with mixed monolayers containing positive molecular dipoles as a way to induce a positive band-edge shift and improve the energetic alignment between $p$-silicon photocathodes and high work function contacting phases. In this presentation, we will report our latest results on the development of new synthetic pathways for the preparation of mixed monolayers on silicon and on the photoelectrochemical properties of $p$-silicon photocathodes functionalized with mixed monolayers.

CP04.04.19
A Comprehensive Study on Mechanical and Thermal Properties of HfSiO$_x$—First-Principles Calculations and Experiments Zhidong Ding, Mackenzie Ridley, Jeroen Deijkers, Md Shafkat Bin Hoque, John Gaskins, Patrick Hopkins, Haydn Wadley, Elizabeth Opila and Keivan Esfarjani; University of Virginia, Charlottesville, Virginia, United States.

HfSiO$_x$(hafnon) can be used as a layer as a barrier coating (EBC) materials placed between silicon dioxide and hafnia. Hafnon has a good lattice thermal expansion matching between silica and hafnia and can prevent oxygen diffusion in EBCs, thereby potentially lengthening the lifetime of EBCs. In this work, we conduct a comprehensive investigation of mechanical, thermodynamic and thermal transport properties of hafnon using first-principles density functional theory (DFT) calculations and compare our results to experiments performed on this material. The volumetric coefficients of thermal expansion (CTE) calculated by the quasi-harmonic approximation are in the range 9.18 \(-19.07\times10^{-6}$ K$^-1$, when the temperature increases from 300 to 1500 K, in agreement with X-Ray Diffraction and dilatometer measurements. The thermal conductivity is nearly 10 Wm$^-1$K$^-1$. The mechanical properties, such as bulk modulus and elastic constants are also compared between the first-principles calculations and the RT nonindentation technique. This study validates our computational approach and can be used to further study thermomechanical properties of other high-temperature oxides.

CP04.04.20
Molecular Interactions of Polydimethylsiloxane and Ni-Mn-Ga Jaime D. Guevara Rojas$^{1,2}$, Matthew L. Jones$^{2}$, Eric Jankowski$^{3}$ and Peter Müllner$^{2}$; $^{1}$Computer Science, Boise State University, Boise, Idaho, United States; $^{2}$Materials Science and Engineering, Boise State University, Boise, Idaho, United States.

Medical micropumps that utilize Magnetic Shape Memory (MSM) alloys are small, powerful alternatives to conventional pumps because of their unique pumping mechanism. This mechanism, the transfer of fluid through the emulsion of esophagae contractions, is enabled by the magneto-mechanical properties of a shape memory alloy and a sealant material. Because the adhesion between the sealant and the alloy determines the performance of the pump and because the nature of this interface is not well-characterized, an understanding of sealant-alloy interactions represents a fundamental component of engineering better solid state micropumps in particular, and metal-polymer interfaces in general. In this work we develop computational modeling techniques for investigating how the properties of sealant materials determine their adhesive properties with alloys. In particular, we develop a molecular model of the sealant material polydimethylsiloxane (PDMS) and parameterize its interactions with Ni-Mn-Ga alloy surfaces for use in molecular dynamics simulations. We perform equilibrium molecular dynamics simulations of the PDMS/Ni-Mn-Ga interface to iteratively improve the reliability, numerical stability, and accuracy of the models and associated data workflows. In sum, we develop a model combining OPLS-UA and UFF force fields for simulating PDMS/Ni-Mn-Ga interfaces and demonstrate its promise for informing the design of more reliable MSM micropumps.

CP04.04.21
Pinning Strength Quantification of Different Solute Concentrations at Grain Boundaries David W. Jacobson$^{1,2}$, Stephen Foiles$^3$, Fadi Abdeljawad$^3$ and Gregory B. Thompson$^4$; $^{1,2}$Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama, United States; $^3$Sandia National Laboratories, Tuscaloosa, Alabama, United States; $^4$Mechanical Engineering, Clemson University, Clemson, South Carolina, United States.

A computational method has been developed to calculate the pressure required for grain boundaries to overcome the pinning effects of second phase particles. Multiple Pt bicrystals were constructed with small concentrations (\(< 0.5 \text{ atom}\%\)) of Au segregated to the boundary using the Monte Carlo method. Molecular dynamics (MD) simulations employing the artificial driving force method were carried out on said boundaries to measure the relationship between boundary type, solute concentration, and boundary velocity. It was found that for a given solute concentration there exists a critical driving pressure necessary for grain boundary motion to occur. Sub-critical driving pressures resulted in flexing of the grain boundary about the pinning precipitates, but with no large scale grain boundary movement. Above critical driving pressures resulted in grain boundary motion although the amount of time required for grain boundaries to break loose from the pinning structures varied considerably. At solute concentrations of 0.1\%, solute segregation to the boundary was not apparent. The resulting lack of precipitation caused the boundaries to behave no differently from pure boundaries, although at high temperatures a reduction in mobility would be exhibited because of solute drag. Development of a method to quantify the effect of different solute concentrations on the stability of different grain boundaries will prove useful for understanding phenomena such as abnormal grain growth, as well as aid in the engineering of stabilized nanocrystalline alloys.

CP04.04.22
Atomistic Measurement of Energy of Ice Grain Boundary and the Ice-Metal Interface Yipeng Peng, Hang Li, Rielessavaine Ji and Liming Xiong; Aerospace Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

The ice accretion on metal surfaces in cold environments occurs through the process of water droplets freezing, which spans a wide range of length scales necessitates a multiscale computational analysis that can link the atomic-scale activities to its micrometer-level behavior.

A computational method has been developed to calculate the pressure required for grain boundaries to overcome the pinning effects of second phase particles. Multiple Pt bicrystals were constructed with small concentrations (\(< 0.5 \text{ atom}\%\)) of Au segregated to the boundary using the Monte Carlo method. Molecular dynamics (MD) simulations employing the artificial driving force method were carried out on said boundaries to measure the relationship between boundary type, solute concentration, and boundary velocity. It was found that for a given solute concentration there exists a critical driving pressure necessary for grain boundary motion to occur. Sub-critical driving pressures resulted in flexing of the grain boundary about the pinning precipitates, but with no large scale grain boundary movement. Above critical driving pressures resulted in grain boundary motion although the amount of time required for grain boundaries to break loose from the pinning structures varied considerably. At solute concentrations of 0.1\%, solute segregation to the boundary was not apparent. The resulting lack of precipitation caused the boundaries to behave no differently from pure boundaries, although at high temperatures a reduction in mobility would be exhibited because of solute drag. Development of a method to quantify the effect of different solute concentrations on the stability of different grain boundaries will prove useful for understanding phenomena such as abnormal grain growth, as well as aid in the engineering of stabilized nanocrystalline alloys.
shown that the contact angle decreases when the volume fraction of the ice crystals in a water droplet increase.

**CP04.04.23**

**Studies in the Ultrathin Tungsten Oxide Layers**

Michael W. Martínez-Szczweczyk, Chandler W. Cotton, Sumner B. Harris and Renato P. Camata;

Physics, University of Alabama at Birmingham, Birmingham, Alabama, United States.

Ultrathin transition-metal oxide and dichalcogenide layers ranging from monolayer (2D) thickness to a few nanometers, exhibit a wide range of distinct physical properties when compared to their bulk counterparts. There is growing interest in understanding the crystallization behavior of these materials when approaching the 2D regime, in order to optimize the growth of already observed phases and realize the synthesis of predicted ones. Information on nucleation rates and critical nucleus size in homogeneous nucleation processes, the relative importance of various defects in heterogeneous nucleation, grain growth rates, and interface evolution in the 2D regime is highly sought to enable interface engineering in 2D materials. Tungsten trioxide (WO3) is a particularly interesting system to study in ultrathin configurations because it exhibits a wealth of crystallization-dependent properties. In addition to its catalytic and ion-intercalation derived properties, such as charge storage and electrochromic behavior, it also shows evidence of a superconducting phase, an insulator-to-metal transition that may be achieved via electrostatic gating, and a transition from the conventional monolonic, orthorhombic, and hexagonal polytypes observed in bulk and nanostates, to a stable free-standing, 2D single-layer honeycomb-like structure that is semiconducting and predicted to have a very high cohesive energy (10.5 eV) as well as one of the highest in-plane stiffness among metal oxide and dichalcogenide 2D materials (250 N/m). In this work we investigate the crystallization behavior of ultrathin WO3 formed after oxidation of tungsten (W), using X-ray diffraction (XRD), atomic force microscopy (AFM), and impedance spectroscopy (IS). Polycrystalline W films of 10-nm thickness, deposited by atomic layer deposition (ALD) on n-type (001)-oriented silicon substrates, were annealed in oxidizing environment in a tube furnace at temperatures from 275°C to 600°C. XRD on films annealed at 600°C shows the formation of the monolonic phase of WO3. The XRD patterns for annealed films are dominated by the sharp monoclinic (200) reflection at 2θ = 24.45°, indicating that the WO3 crystallites exhibit preferential orientation with their [001] axis aligned perpendicular to the substrate. AFM shows surface morphology comprising distorted cubic-like features consistent with the underlying monoclinic structure observed by XRD. The AFM scans clearly reveal that the films are dominated by out-of-plane interfaces normal to the [200] direction of the WO3 crystallites. At temperatures above 500°C, large crystallites are observed in the AFM scans, with heights in the 10-30 nm range, indicating significant 3D restructuring due to crystal growth after oxidation. The crystallite number density exhibits an Arrhenius relationship with the annealing temperature with an activation energy of 110 kJ/mol. Impedance spectroscopy measurements between 1 Hz and 7 MHz on thin film samples after the deposition of top nickel contacts, show Nyquist impedance arcs that depend on the annealing temperature and ambient. The impedance of samples with various WO3 thicknesses, degrees of 3D restructuring, and crystallite number densities are analyzed in terms of equivalent circuits that yield the “grain interface” and “grain interior” contributions to the resistance and capacitance of the samples. The dependence of these electrical characteristics is compared with the structural features obtained by XRD and AFM to identify distinct kinetic regimes present during W oxidation, as well as crystal nucleation and WO3 ultrathin layers.

**CP04.04.24**

**Investigation of Light Emission and Scattering Properties of a Racemic Mixture of Helicene Derivative Deposited on Plasmonic Substrates Using Scanning Tunneling Microscope (STM)**

Pawel Krukowski, 1, 3 Sungeol Cha, 1, 2 Hideji Osuga, 2 and Yuii Kuzuhara; 2 Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Japan; 3 Department of Materials Science and Chemistry, Faculty of Systems Engineering, Wakayama University, Wakayama, Japan; 3 Department of Solid State Physics, Faculty of Physics and Applied Informatics, University of Lodz, Lodz, Poland.

In this study we report our investigations of adsorption of a racemic mixture of 2,13-bis(aldehyde)[7]-thiatricothelene (rac-[7]TH-dial) on Au(111), Cu(001), and NiAl(110), as well as the reflection of light emission/scattering from the molecules induced by a STM tip. Light emission from the rac-[7]TH-dial molecules was investigated by STM-induced luminescence (STM-LE), while light scattering was investigated by STM tip-enhanced Raman spectroscopy (STM-TERS) techniques. Helicene molecule belongs to the class of chiral molecules revealing a characteristic helical shape, which comes from steric hindrance between adjacent aromatic rings. All STM-LE and STM-TERS measurements were carried out in ultrahigh vacuum spectrometer using Ag tip. At the beginning, the influence of the substrate on the self-assembly process of rac-[7]TH-dial on Au(111), Cu(001), and NiAl(110) has been studied with the use of standard STM. Despite the same deposition conditions, only Au(111) governed molecular self-assembly formation. We observed a few different phases with highly ordered structures formed on a wide area of the Au(111) surface. The dominant observed structure was characterized by the presence of highly ordered domains ranging from hundreds to thousands of nanometers adsorbed directly on the Au(111) surface. The highly ordered domains consist of self-assembled zigzagged row exhibiting self-assembled rac-[7]TH-dial molecules with orientation and positional order were preferentially aligned parallel to the highly symmetric <1-10> or <11-2> directions. Despite the same deposition conditions, the adsorption of rac-[7]TH-dial on Cu(001) and NiAl(110) surfaces was quite different from that observed on Au(111). The rac-[7]TH-dial molecules on Cu(001) and NiAl(110) formed an amorphous layer with densely packed molecular stacking. As the amount of rac-[7]TH-dial molecules decreased, the formation of randomly distributed clusters of similar sizes become dominant. What is more, we report our STM tip-induced light emission investigation on rac-[7]TH-dial molecules and highlight the strong enhancement of light emission over rac-[7]TH-dial clusters formed on NiAl(110), suggesting the molecular character of light. Additionally, we show evidence of nanoscale dehydrogenation occurring during STM-TERS measurements on rac-[7]TH-dial molecules adsorbed on Au(111) surface. The near-field STM-TERS spectra obtained locally on a self-assembled monolayer of rac-[7]TH-dial molecules showed vibrational frequencies in good agreement with that predicted by density functional theory calculations, except for the L-mode at ~2000 cm⁻¹, which was ascribed to a carbon—carbon triple bond, revealing that the benzene rings had been dehydrogenated during the experiments. We conclude that one side benzene ring was dehydrogenated as a result of pyrolysis, with the Ag tip acting as source of local heat and catalyst.

This work is supported by a Grant-in-Aid for Scientific Research (S) (No. 24221009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and National Science Centre (2017/26/E/ST8/00987), Poland.

**CP04.04.25**

**Mechanistic Understanding of Carburation from First-Principles Simulations**

Ahmed Darwish and Jacob Eapen; Department of Nuclear Engineering, North Carolina State University, Raleigh, North Carolina, United States.

The structural components of a very High Temperature Reactor (VHTR) are exposed to trace amounts of gaseous elements and moisture. These impurities can adversely affect the integrity of the reactor structural components. Among the impurity gases, carbon-bearing gases – methane, carbon monoxide and carbon dioxide – have significant detrimental effects on the protective oxide scales, which grow on nickel-based alloy surfaces, leading to carburation of the alloy.

In this work, we investigate the effect of carburing gases on the stability of chromium oxide scales using electronic structure simulations. We have utilized Kohn-Sham density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) with the generalized gradient approximation; to describe the strong correlations between the d electrons of chromium, we have utilized the DFT+U approach. The molecular structure of the oxide surface without the gases is first optimized structurally. Fully relaxed carburing gases are then allowed to be adsorbed on to the surface. We finally employ ab initio molecular dynamics (AIMD) simulations at high temperatures (up to 1200 K) to calculate the structural and dynamic properties of the interface, and to elucidate the mechanisms of thermal stability of the interface region at different temperatures and impurity coverage of the surface.

**References**


**CP04.04.26**

**Atomic Scale Study of Ordered-Structures Induced by Cu Grain Boundary Segregation at Al 7075 Alloys**

Prakash Parajuli, Ruben Mendoza-Cruz and Miguel J. Yacaman; Physics and Astronomy, University of Texas at San Antonio, San Antonio, Texas, United States.

Segregation of the alloying elements at the Grain boundaries (GBs) in a polycrystalline materials leads to a nanoscale chemical and structural variations along the GB region that can significantly alter the material’s performance. Hence, the experimental investigation of the atomic structure and chemistry of the grain boundaries by resolving the sites and chemical identities of the atoms comprising the interface is crucial to fully understand the implication of the atomic segregation phenomenon. Herein, we present the atomic scale analysis of ordered-structures induced by segregation of Cu atoms in Al 7075 alloy GBs along with the detailed examination of microstructural features (texture and grain boundary character distribution) by employing advanced microscopic characterization techniques: STEM-HAADF imaging, spectroscopic (EDS and EELS) analysis, and scanning
precession electron diffraction (PED). The <111> strong texture and dominant low coincidence site lattice (CSL) GBs were revealed in the films. Results demonstrated the segregation of Cu in all types of GBs, but with varying segregation patterns. Atomic-scale structure of each type of GBs showed two types of Cu GB segregation behaviors namely, point (highly segregated atomic column surrounded by low segregated columns, misorientation < 28°) and parallel array (two highly segregated columns opposite to each other across the interface surrounded by low segregated columns, misorientation > 28°). In addition to the single atom-interstitial hollow site (point) segregation behavior (predicted in theoretical studies and assumed to analyze the segregation effects), subsurface core site segregation of two columns of Cu atoms forming an ordered-structures with a parallel array of segregating atoms along the interface has been demonstrated. This is the first time that this type of parallel array segregation behavior has been reported. Furthermore, based on intensity profiles and scanning transmission electron microscopy Z-contrast principle, non-uniformly (high and low) segregated mixed atomic columns were predicted at the grain boundaries. We believe the knowledge of this type of experimental insight of the atomic scale arrangements of adsorbate on the GBs can potentially help to develop strategies for engineering the design of alloy compositions.

CP04.04.27
Controllable Introduction of Oxygenated Functional Groups into Carbon Materials for Gas Molecule Adsorption Enhancement Xinxin Pu1, Ani Wang2, Zhibin Qu1, Fei Sun1 and Jihiu Gao1; 1School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, China; 2School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, China.
Carbon materials with porous skeleton and specific chemical functionality have shown great potentials in the applications of gas adsorption, storage, separation and sensing. While a variety of literature have demonstrated that pore structure and chemical environment of carbon materials possess synergistic effects on these applications, there is still much to learn regarding structure-activity relationships, especially individually determining the role of chemical functionality or porosity in gas adsorption. Oxygen-containing groups widely exist in carbon materials and profoundly influence gas molecule adsorption on carbon surface, the complexity of carbon source and post-treatment methods, however, modify not only the surface chemistry of carbons but also their porous structure, making it considerably difficult to exclusively determine the effect of O-species. To this end, edge carboxyl group decorated graphene nanoplatelets (OGNPs) were used to investigate the effects of O-species on gas adsorption using SO2 as probe molecule. The OGNPs were obtained employing a simple ball milling method with dry ice assistance by which the oxygen content can reach as high as 14.06 wt-%, allowing 21 times increase in SO2 adsorption capacity as compared with oxygen-free graphene nanoplatelets. Both temperature-programmed desorption (TPD) experiments and DFT calculation were used to elucidate the nature of enhanced SO2 adsorption including adsorption types, adsorption energy and carbon-SO2 interactions. The adsorbed SO2 molecules on OGNPs can desorb easily at temperature lower than 100 °C, indicating their physisorption nature. Based on adsorption energy data, DFT calculation further demonstrate that the enhanced SO2-carbon adsorption by carboxyl groups doping is in the form of physisorption but not chemisorption. This means that the role of oxygen doping is to remodel the local electronic density, the polarity of carbon atoms as well as charge distribution of carbon surface, which induces the enhanced SO2 adsorption.

CP04.04.28
Crystallinity Improvement of Mist Chemical Vapor Deposition Grown ZnO Thin Films by Controlling Film Crystal Orientation Phimolphan Ruthongjan1, Misaki Nishi1, Li Liu1, T. Dang1 and Toshiyuki Kawaharamura1; Kochi University of Technology, Kochi, Japan.
Zinc oxide (ZnO) is one of promising semiconductors for numerous (opto)electronic applications because of excellent properties such as a wide band gap, a high exciton binding energy, and large piezoelectric coupling coefficients. ZnO crystallizes in the wurtzite hexagonal structure, which forms the polar c-plane and non-polar a and m planes. ZnO thin films of different preferential crystal orientations exhibit different properties, which leads to various applications. In ZnO films grown by chemical vapor deposition (CVD) techniques, the crystal orientation is mainly influenced by the orientations of the nucleation layer, which is, in turn, affected by diffusion of atoms along the surface during film growth. Several parameters affect the diffusion process such as oxidation reactions, type of substrates, growth temperatures, and gas flow rates. In the growth of metal oxide films by CVD, oxidation rate can be controlled by varying the supply amounts of oxygen and metal sources. Mist-CVD is one of the non-vacuum metal oxide film growth techniques capable of controlling the oxygen and metal supply amounts precisely. The precise control of the oxygen/metal ratios was realized by using the mist-CVD system with two solution chambers storing oxygen and metal sources (H2O and Zn precursor in this case) separately. In this work, we found strong dependences of the crystal orientations, growth rates, and surface morphologies on the [H2O]/[Zn] ratios in the ZnO films grown by the two chamber system. The equilibrium reaction of thermal decomposition of the Zn precursor was enhanced by addition of H2O leading to an initial increase in the growth rate with the [H2O]/[Zn] ratio. However, excessive addition of H2O caused a decrease in the growth rate. Moreover, H2O also influences the film crystal orientation. The diffusion of zinc and oxygen reactive atoms on the substrate surface during film formation was influenced by the [H2O]/[Zn] ratios, which resulted in different ZnO preferential growth orientation and film surface morphology.

CP04.04.29
Atomistic Modeling of Ionic Liquid Mixtures as Electrolytes in Electrochemical Capacitors Alta Fang and Alex Smolyanitsky; National Institute of Standards and Technology, Boulder, Colorado, United States.
Electric double-layer capacitors (EDLCs), also known as supercapacitors, are energy storage devices that deliver high power densities and long cycle lives but exhibit lower energy densities than Li-ion batteries. Improving the energy density of EDLCs without sacrificing their power density or lifetime is desirable for numerous energy storage applications. In order to rationally design higher energy and power density devices, an improved understanding of how electrolyte and electrode properties affect the performance of EDLCs is critical. Recently the use of ionic liquid mixture electrolytes as has been experimentally reported to improve EDLC performance under certain conditions. However, existing theoretical and computational work on ionic liquid mixtures in EDLCs remains limited, and there remains a need for detailed understanding of how ionic liquid mixture electrolytes affect EDLC performance. Using all-atom molecular dynamics simulations, we study the nanoscale adsorption behavior of mixtures of ionic liquids comprised of 1-ethyl-3-methylimidazolium (EMIM+), bis(trifluoromethylsulfonyl)imide (TFSI-) and tetrafluoroborate (BF4-) ions near planar carbon electrodes carrying surface charges that mimic externally applied voltages. Near uncharged electrodes, we find that ion-electrode interaction Waals interactions have a significant impact on the relative population of different ions in the first interfacial layer. By characterizing ion densities within a few nanometers of charged electrodes, we find that charging of the electrodes leads to greater overall changes in cumulative density of the smaller ion in each pure ionic liquid compared to the larger ion, as the larger ions tend to instead reorient and locally restructure close to the interface. Finally, in ionic liquid mixtures we identify an effective anion exchanging phenomenon near negatively charged electrodes that enhances counter-ion adsorption and provides a mechanism for capacitance enhancement. More broadly, our observation of modest capacitance differences between the ionic liquid compositions suggests that achieving substantially higher energy densities will ultimately also require tuning the structure and properties of the electrodes.

CP04.04.30
Ag Thin-Film Coating on LiCoO2 Electrodes for a Stable Solid-Electrolyte Interface at High-Voltage Operations Taner Zerrin, Congiz S. Ozkan and Mihrimah Ozkan; University of California, Riverside, Riverside, California, United States.
Increasing the operation voltage of LiCoO2 (LiC) is a direct way to enhance the energy density of the Li-ion batteries. However, overcharging the cells results in a very fast degradation of cycling stability due to the irreversible solid-electrolyte interface layer. In this work, Ag thin film was prepared on commercial LCO cathode by using magnetron sputtering technique to modify the interface between electrode and the electrolyte. Various electrochemical and
physical characterizations were performed to understand the diffusion kinetics of Li ions at the electrode-electrolyte interface. Coating the electrode surface with Ag thin film delivers an improved Coulombic efficiency, which is an indication of suppressed parasitic reactions at the electrode surface. As a result of the surface modification, Ag coated electrode enables an improved electrochemical performance with a much better cycling capability compared to that of the uncoated electrode. This work may lead to new methods on the interface modifications of LCO and other electrode materials to achieve high-capacity Li-ion batteries at high-voltage operations.

**CP04.04.31**

**Molecular Dynamics Simulation and Disconnection Model for Faceting of Migrating Grain Boundaries**

Larissa Woryk\(^1\), Spencer Thomas\(^1\), Jian Han\(^1\), Kongtao Chen\(^1\) and David Srolovitz\(^2,3\)

\(^1\)Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; \(^2\)Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong.

Grain boundaries (GBs) migrate via the motion of disconnections (line defects in the GB that have both step and dislocation character). While the motion of symmetric tilt boundaries via this mechanism is reasonably straightforward, application to more general GBs requires additional assumptions. In this poster, we report the results of molecular dynamics (MD) simulations of the motion of asymmetric GBs. In particular, we examine the faceting of migrating asymmetric GBs. In some cases, faceting may occur during migration even when no faceting is observed in the stationary case. We analyze the MD results in the context of a disconnection description of GB migration. Finally, we discuss implications of dynamic GB faceting on grain growth.

**CP04.04.32**

**Thermotropic Polymers with Robust Interfaces for Transparency-Tunable and Impact-Resistant Windows**

Cheng Zhang and Jian Lin

The University of Missouri, Columbia, Missouri, United States.

Thermotropic polymers own thermally tunable transparency which have shown applications in intelligent solar control coating, privacy windows, displays, and optical/thermal sensors. Usually, thermotropic polymer systems are constructed by physically dispersing phase transition materials in transparent hosting materials. However, they usually possess bad interfaces either between the dispersion and the matrix, or between the thermotropic system and the supporting substrates (e.g., glass), resulting in poor mechanical properties, weak interfaces to substrates, or bad long-term stability. Herein, we demonstrate a novel chemically interconnected thermotropic polymer, which is obtained by reacting dodecanedioic acid (DDA) with glycerol. In the system, some of DDA molecules were crosslinked to form a polyester network, poly(glycerol-dodecanoate) (PGD). Other grafted but non-crosslinked DDA molecules form semi-crystalline domains which possess a solid-liquid phase transition within the PGD matrix. The phase transition offers the resulting hybrid materials with tunable optical transparency. In addition, when applied for window coating, it results in tough interfacial bonding to glass substrates with toughness of > 6910 J m\(^{-2}\) below its transition temperature and > 153 J m\(^{-2}\) above its transition temperature. It increases the impact-resistance of the window by multiple times.

**CP04.04.33**

**Multimodal Chemical and Functional Imaging of Functional Materials via Combined AFM/ToF-SIMS Platform**

Anton V. Ievlev

Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

For the last several decades Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) became a prime tool for chemical characterization of wide range of materials and systems with sub-micrometer spatial and nanometer depth resolution. However, it lacks characterization of the morphological, physical and functional properties of the studied sample. This issue can be addressed by combination with Atomic Force Microscopy (AFM). Such combined multimodal AFM/ToF-SIMS platform enables a nanoscale characterization of both chemical and physical properties of the sample along with its surface morphology. In this case, chemical information acquired by the ToF-SIMS can be correlated with functional response measured by the AFM. Furthermore, it opens pathway for chemical characterization of the local materials behavior on the nanoscale, when local chemical phenomena induced by the physical fields of the AFM tip (e.g. mechanical or electric) are characterized by the ToF-SIMS.

Here we utilize commercial AFM/ToF-SIMS platform to explore interplay of chemical and physical properties in ferroelectrics during polarization switching in lead zirconate titanate (PZT, Pb(Zr\(_{0.52}\)Ti\(_{0.48}\))O\(_{3}\)) thin films. Using this multimodal imaging platform, we demonstrated that chemical phenomena plays significant role in ferroelectric switching process. Specifically, we found that local ferroelectric switching by the AFM tip, significantly alters the chemical composition in the 3-mm-thick surface layer of the sample, forming reversible concentration wave, of Pb\(^+\) ions. Furthermore, investigations of the polarization cycling in the PZT sample with copper electrodes, showed penetration of the copper cations deep into the PZT structure. This explains ferroelectric fatigue phenomenon, leading to decrease in spontaneous polarization during spontaneous polarization cycling.

Additionally, explored chemical phenomena associated with ferroelectric switching will enhance fundamental understanding of ferroelectric phenomena and aid in the practical application of ferroelectrics in devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility and using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

**CP04.04.37**

**Using Light to Regulate Adhesion of Polymers to Substrate**

Hossein Mostafavi\(^1\), Kyle Clark\(^1\), Miranda Sroda\(^1\), Javier R. Alanz\(^2\) and Chris Bardeen\(^1\)

\(^1\)Chemistry, University of California Riverside, Riverside, California, United States; \(^2\)Bioengineering, University of California, Riverside, Riverside, California, United States.

One of our goals in Bardeen’s group is to explore the possibility of using photochromic molecules to regulate photo-adhesion. We have used various molecules including spiropyran, DASA (donor–acceptor Stenhouse adducts) and aracenes. These photochromic molecule shows new properties under light irradiation.

In one of our first projects we have used spiropyran (SP) molecules to increase adhesion of thin films of polystyrene (PS) to glass substrate. We have shown that photochromic reactions of SP doped in PS can significantly enhance the adhesion of PS to a glass surface. Shear adhesion test studies demonstrated that adhesion of polystyrene to glass slides increased by factor of 7 after irradiation. We hypothesize that the adhesion changes arise from localized polymer and molecular motions that eliminate void spaces and surface gaps at the polymer–glass interface. The results show that adhesive forces between a prototypical polymer and an inorganic substrate can be modulated by photochromic reactions of embedded molecules.

In the next studies we have used DASA molecules that has different properties compared to spiropyran. In Contrast with Spiropyran, DASA molecule is negative photochrome and its volume reduced after laser irradiation. This is in opposite direction of what we observed for spiropyran and we expected to see a decrease in adhesion of films to surface. We have used three different methods to measure adhesion before and after laser irradiation including water detachment, adhesion test and shear test and in all samples the adhesion decreased. Our experiments suggest that molecules’ photo induced shrinking may increase voids and pores and these changes will leads to a decrease in adhesion. Reduction of chemical interaction of molecules to surface may be another reason for this change.

As an application we tried to encapsulate organic dye -as a mode -between two glass surfaces which glued together by PS/DASA polymer. Then we measured time that the adhesion would break in water and irradiated samples released dyes 10 times faster than non-irradiated samples.

In conclusion we showed that we can remotely increase and decrease adhesion using various photochromics.

**CP04.04.38**

**Shedding Light onto the Controversy Around Graphene Wettability Opacity by Locally Probing Surface Free Energy**

Matteo Chiessi and Jin-You Lu

Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates.

Understanding how graphene coatings modify the surface free energy of a substrate is essential when implementing graphene in device fabrication and operation. Intensive recent studies report the partial wetting transparency of graphene, suggesting that the wettability of graphene is partially governed by the underlying substrate and becomes more hydrophobic with increasing the number of graphene layers for hydrophilic surfaces. However, a number of studies argue against the wetting transparency of graphene, indicating that monolayer graphene coating significantly dominates the surface wettability. Despite argument between proponents of graphene wetting transparency and opacity, a common denominator among these studies is the extensive use of static water contact angle (WCA) measurements for characterizing the graphene surface energy. Traditionally, the contact angle of a liquid droplet on homogeneous solid surfaces has been used to provide a quantitative measure of the surface properties of bulk solid surfaces, such as polymer, Si/SiO\(_2\), and different metal surfaces. However, the use of this macroscopic WCA in the study of graphene wettability has led to controversial measurements due to the complexity of
graphene coatings, where factors including the quality of graphene growth, transfer process, water adsorption, and hydrocarbon contaminants all impact the apparent surface properties. Specifically, macroscopic WCA techniques require large scale surface coverage of graphene to contact the milliliter size water droplet at the solid/liquid interface. This is challenging since one cannot precisely control the number of graphene layers at the contact line. In addition, for transferred graphene coatings, it is difficult to maintain consistent measurement results due to possible inhomogeneous contamination during the transfer process. These challenges are often ignored despite being the origin of the uncertainty in the measurements that have led to many contradictory interpretations.

In order to shed light into this controversy, we propose combining high resolution bimodal atomic force microscopy (AFM) with micro-Raman spectroscopy to measure the surface energy of graphene on SiO$_2$ substrates. Resolution and qualification of atomic force microscopy characterization are enhanced by forcing the AFM tip to oscillate near the solid surface in ambient in small amplitude and small set-point (SAAS) operation mode. Several physical quantities related to surface properties, such as force of adhesion, Hamaker constant, and elastic modulus, can be efficiently and statistically extracted from the feedback of observable raw parameters. In this work, we are particularly interested in exploring the adhesion force on the graphene surface since it is directly related to its surface free energy.

Two different families of graphene coatings: CVD-grown graphene and exfoliated graphene, are transferred to SiO$_2$ coated silicon wafers using a wet etch process and micromechanical cleavage technique, respectively. Unexpectedly, the surface free energy derived from AFM force of adhesion shows two opposite trends. The exfoliated samples show graphene being partially transparent by the underlying substrate, which supports graphene partial transparency theory. The other CVD-grown samples show that graphene is non-transparent and insensible to the underlying substrate, which supports the van der Waal opaque theory proposed by recent AFM characterization results on graphene/SiO$_2$ and MoS$_2$/SiO$_2$. By averaging the Raman measurements, the interface between graphene and SiO$_2$ substrate is identified to dominate the difference of observed surface free energy between exfoliated and CVD-grown graphene on SiO$_2$. Moreover, in addition to quantitatively estimation of surface energy change with different number of graphene layers, two levels of theoretical analysis using ab initio density functional calculations support our experimental observations.

SESSION CP04.05: Interface Motion
Session Chairs: Srikanth Patala and Timothy Rupert
Wednesday Morning, April 24, 2019
PCC West, 100 Level, Room 102 A

8:00 AM *CP04.05.01
**Triple-Junction Dynamics During Grain Boundary Migration**
David J. Srolovitz$^{1,2,3}$, Spencer L. Thomas$^2$, Jian Han$^2$, Chaozhen Wei$^3$ and Yang Xiang$^3$; $^1$Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong; $^2$Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; $^3$Institute for Advanced Study, The Hong Kong University of Science and Technology, Kowloon, Hong Kong; $^4$Hong Kong Institute for Advanced Study, City University of Hong Kong, Kowloon, Hong Kong; $^5$Mathematics, The Hong Kong University of Science and Technology, Kowloon, Hong Kong.

Grain boundaries (GBs) move by the formation and propagation of disconnections; line defects with both dislocation and step character. During the evolution of a polycrystalline microstructure, disconnections pile-up against triple junctions (TJs). This implies that TJs accumulate a net Burgers vector, $\mathbf{B}$. As the GBs migrate, the net Burgers vector at the TJ grows, creating a back stress that effectively shuts off additional disconnection motion and stops GB migration. TJs have many options to relax the Burgers vector and back stress: (1) accumulation of cancelling disconnection from the other GBs meeting at the TJ, (2) emission of other defects (e.g., lattice dislocations, twins,...), and (3) formation of new types of disconnections along the GB with opposite sign Burgers vector. I will show molecular dynamics simulations, theoretical analysis, and continuum simulations that show what is going on at TJs during GB migration and examine its implications for microstructure evolution.

8:30 AM *CP04.05.02
**Shear Induced Motion of Twin Boundaries in Mg via Disconnection Terrace Nucleation, Growth and Coalescence**
Douglas E. Spearot$^1$, Laurent Capolungo$^3$ and Carlos Tome$^4$; $^1$Univ of Florida, Gainesville, Florida, United States; $^2$Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Twinning is a common deformation mode in hexagonal close packed metals such as magnesium. This atomistic simulation study characterizes the relationship between the kinetics associated with motion of the \{10-12\} twin boundary in pure Mg and the nucleation, growth and coalescence of disconnection terraces on the twin boundary. This problem is resolved adopting both 2D and 3D simulation geometries. This study shows that the kinetics of twin boundary migration can only be addressed in 3D, as 2D simulations predict twin boundary migration rates at least an order of magnitude higher than 3D simulations. A simple constitutive relationship is extracted from the atomistic simulations. Such a model, accompanied by observations of disconnection terrace nucleation, growth and coalescence, reveals the existence of an autocatalytic terrace nucleation regime for the shear induced motion of the \{10-12\} twin boundary in Mg.

9:00 AM *CP04.05.03
**A Machine Learning Exploration of Grain Boundary Mobility Mechanisms**
Leila Khalili$^1$, Eric R. Horner$^2$ and Srikanth Patala$^3$; $^1$Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; $^2$Department of Mechanical Engineering, Brigham Young University, Provo, Utah, United States.

The mobility of grain boundaries plays an important role in governing the kinetics of microstructural evolution in every class of polycrystalline materials. Of particular interest is the role of bicrystallography, characterized by the macroscopic crystallographic degrees of freedom, on the underlying atomistic mechanisms governing grain boundary mobility. In this talk, I will present an algorithm to automatically identify the atomistic motion mechanisms that give rise to mobility of an interface. We use machine-learning methods, inspired by recent work in disordered solids, to correlate local structure with the susceptibility for rearrangement of grain boundary atoms. We show that it is possible to automatically identify mobility mechanisms of grain boundaries with a diverse range of crystallographic character.

9:30 AM BREAK

SESSION CP04.06: Surface-Driven Phenomena
Session Chairs: Wendy Gu and Timothy Rupert
Wednesday Morning, April 24, 2019
PCC West, 100 Level, Room 102 A

10:00 AM CP04.06.01
**First Principle Study of the Protonation Effect and Active Sites Towards Oxygen Reduction Reaction on α-MnO$_2$(211) Plane**
Xium Shu, AM Kannan and Xihong Peng; Arizona State University, Mesa, Arizona, United States.

The most commonly believed oxygen reduction reaction path on α-MnO$_2$ plane in alkaline media is undergoing water uptake or protonation to form MnOOH, then adsorb the oxygen. In this study, first-principles density functional theory calculations were used to simulate the oxygen adsorption on the clean α-MnO$_2$(211) plane and the protonated plane. There are total four possible sites at which the proton will bond with oxygen, all the proton adsorption energy is ~2 eV with a tiny variation. Total eight possible configurations were considered for oxygen adsorption onto the α-MnO$_2$(211) plane, include O=O=O, O=O−O=Mn and Mn−O=O=Mn sites. All the configurations showed oxygen adsorbed to the surface, with the adsorption energy ranging from 0.27−1.76 eV. The theoretic optimized oxygen adsorption is ~1.8 eV. The Mn−O=O=Mn sites showed the best improvement with protonation among all the O=O−O, O=O=O=Mn sites. The bond length for Mn−O=O=Mn sites doesn’t change very much with protonation.
Semiconductor photoelectrodes for hydrogen generation in photoelectrochemical cells are a very good demonstration example for the role which defects can play in function of electrical devices.

We present an extensive study on metal oxide heterostructures synthesized by chemical deposition methods with soft x-ray spectroscopy and electroanalytical methods. The matching of substrate current collector and photoabsorber layer forms an interface with a malignant electronic defect state which can be "healed" by introduction of a buffer layer from a different metal oxide - to the extent that the performance of the photoelectrode increases considerably. The molecular origin of this effect is uncovered by using oxygen ligand spectroscopy with soft x-rays. Specifically, a malignant state in the valence band at the interface is removed upon introduction of the buffer layer. The charge transport increases accordingly.

Different roles of defects are necessary at the surface which is in contact with a liquid electrolyte. Here the electrocatalytical properties are relevant, and correspondingly the absorber material is facing a challenge which its stoichiometry can not perform well. But a chemical after processing step, specifically gas phase reduction alters the oxidation state of the surface of the absorber to an extent that it can increase the photocurrent and hydrogen production efficiency considerably. This is evidenced both with soft x-ray spectroscopy and electron spectrscopy.

With this study is shown how the proper processing of components in heterostructures can yield better component performance in a device and thus better device performance.


10:30 AM CP04.06.03
Time Resolved Ambient Pressure X-Ray Study of Li$_2$CO$_3$ Formation on Garnet Electrolyte in CO$_2$ Melling Sun 1, 2; Yierpan Aierken 1, 3, Ane Etxebarria 1, 3, Hao Shen 1, David Prendergast 1, 2, Marca M. Doet 1 and Ethan J. Crumlin 1; Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3CIC Energigune, Parque Tecnológico de Álava, Múgica, Spain; 4Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Garnet Li$_2$La$_2$Zr$_2$O$_7$ (LLZO) has been considered as one of the most promising solid-state electrolytes that could enable solid-state-batteries employing metallic Li anodes. However, most Li$_x$A$_2$M$_2$O$_7$ garnets have been reported to react with air or moisture, which results in the loss of Li and also in the appearance of a main Li$_2$CO$_3$ secondary phase that is detrimental to the Li$^+$ conductivity at the Li$_2$-LLZO interface. Interestingly, different to other garnets, cubic LLZO was recently reported to be more stable in humid atmosphere regarding no structure change and conductivity degradation upon exposure to humid atmospheres. Although it is known that generally Li$^+$/H$^+$ exchange took place when garnet expose to moisture, the mechanism of how Li$_2$CO$_3$ forms on the interface is still unclear, especially for cubic LLZO. There is also lack of study on the independent role which CO$_2$, H$_2$O and O$_2$ play roles in Li$_2$CO$_3$ formation. Here we performed time resolved Ambient-Pressure X-ray Photoelectron Spectroscopy to monitor Li$_2$CO$_3$ thickness growth kinetics on Al-doped cubic LLZO in the presence of dry CO$_2$, O$_2$ assisted CO$_2$, and H$_2$O. CO$_2$ moisture under different gas pressures (0.01 mTorr, 1 mTorr, 100 mTorr). We elucidated that small amount of O$_2$ significantly catalyzes the Li$_2$CO$_3$ formation on cubic LLZO. Moreover, the minimal Li$_2$CO$_3$ formed in humid CO$_2$ when expose to three atmospheres of 100 mTorr, probably went through COOH$^-$ generation and is due to proton blocking effect. We hope this kinetic spectroscopic study would shed light on protecting carbonation of LLZO during processing and help to further understand the Li$_2$CO$_3$ formation mechanism in different gases.

ACKNOWLEDGEMENTS: The authors thank funding from the Energy Biosciences Institute and Shell International Exploration and Production Company. This research used resources of the Advanced Light Source, which is a U.S. Department of Energy, Office of Science User Facility under contract no. DE-AC02-05CH1231. The synthesis used the facilities supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Portions of the calculation work were supported by a User Project at The Molecular Foundry and its compute cluster (vulpus), managed by the High Performance Computing Services Group at Lawrence Berkeley National Laboratory (LBNL), and portions of this work used the computing resources of the National Energy Research Scientific Computing Center, LBNL, both of which are supported by the Office of Science of the United States Department of Energy under Contract DEAC02-05CH1231.

10:45 AM *CP04.06.04
Coupling Chemistry and Mechanics in Nanomaterials Joerg Weissmüller 1, 2; Hamburg University of Technology, Hamburg, Germany; 1Helmholtz-Center Geesthacht, Geesthacht, Germany.

Many materials phenomena contain signatures of the coupling between chemistry (or electrochemistry) and mechanics. The coupling in the bulk of alloys is well acknowledged, for instance in studies of coherence phase transformations or of damping phenomena. Yet, strong coupling phenomena can also be found at interfaces. This may be exploited in novel materials concepts that afford unexpected functional behavior. Nanoporous-metal based hybrid materials that behave similar to piezoelectric ceramics exemplify this concept: Bodies of nanoporous gold impregnated with electrolyte emit exceptionally robust electric signals when subjected to external load. The metal-based material may thus be considered as piezoelectric, in a literal interpretation of the term. A predictive understanding of the interfacial stress-charge coupling, as the underlying microscopic phenomenon, remains elusive even after systematic experimental and numerical studies. On the other hand, the concepts which have been established in the discussion of bulk chemo mechanical coupling provide useful insights into a related phenomenon, namely the coupling between adsortion enthalpies and strain. This topic is of high interest to the field of strain-modulated catalysis. The talk will discuss relevant issues from the perspectives of experiment, phenomenological thermodynamics, and atomistics.

11:15 AM CP04.06.05
Surface Dominated Deformation in Sub-10 nm Au Nanocrystals at High Pressure Wendy Gu and Abhinav Parakh; Stanford University, Stanford, California, United States.

Sub-10nm metallic nanocrystals are expected to have unique elastic properties, strength and deformation due to the close proximity of surfaces, but are challenging to study due to the small forces and dimensions involved. Here, we use a diamond anvil cell to deform metallic nanocrystals under quasi-hydrostatic, and non-hydrostatic pressure up to 20 GPa in order to determine deformation mechanisms in this size regime and their dependence on microstructure. In particular, we are interested in the processes that lead to pseudoelasticity, or reversible shape recovery from large strain, that have been observed previously in small noble metal nanocrystals. Au nanocrystals with sizes from 4-10 nm are synthesized using colloidal methods. Structural changes under pressure are measured using optical absorbance spectroscopy and high pressure X-ray diffraction. Optical absorbance spectroscopy is used to monitor plasmonic resonance, which is highly sensitive to nanocrystal size and shape. High pressure X-ray diffraction reveals changes in the position and breadth of diffraction peaks, which reveals elastic strain, microstrain and the formation of crystalline defects. These measurements are corroborated by transmission electron microscopy on nanocrystals after compression. We find that 4nm Au nanocrystals are able to reversibly recover their size and shape after load is removed, even after compressed of ~20% along one axis. Crystalline defects remain in the nanocrystals after recovery. Larger Au nanocrystals do not exhibit this pseudo-elastic shape recovery.

11:30 AM CP04.06.06
Multi-Resolution Characterization of Surface Topography for Improved Prediction of Surface Properties Tevis D. Jacobs1, Abhijeet Gujrati1, Luke A. Thimons2, Subarna R. Khanal1 and Lars Pastewka1; 1Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 2University of Freiburg, Freiburg, Germany.

Surface topography strongly affects the functional performance of free surfaces. For example, in electromechanical switches and other applications that make and break contact, surface topography affects the mechanical and transport properties of the contact. Further, in coatings applications, the adhesion of thin films depends strongly on the surface topography of the coated surface. However, many experimental investigations to quantify the effect of surface topography on properties are inconclusive. This is because most surfaces have multi-scale fractal-like roughness, such that the values of measured topography parameters depend on the characterization size and method.
Here we use nanocrystalline diamond films of varying grain size as model systems to investigate the quantitative connection between surface structure and surface properties. In the first part of the talk, we demonstrate the quantitative characterization of surface topography using transmission electron microscopy and its combination with conventional techniques for multi-resolution characterization. Specifically, more than 100 individual measurements at scales from Ångströms to centimeters are combined using spectral analysis to yield scale-dependent information on surface and interface topography. In the second part of the talk, we discuss multi-resolution measurements of adhesion as a function of topography. Results are analyzed in the context of multi-scale continuum mechanics models. The investigation demonstrates that this multi-resolution approach to topography characterization is far more effective than any conventional (single-scale) roughness descriptors at predicting adhesion and other surface properties.

SESSION CP04.07: Radiation and Interfaces
Session Chairs: Julie Cairney and Mitra Taheri
Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 102 A

1:30 PM CP04.07.01
Grain Boundary Metastability Under Irradiation—Toward Tunable Sink Efficiency
Mitra Taheri, Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States.

Understanding the sink efficiency of interfaces under irradiation is of paramount importance to tailoring materials for radiation tolerance. Using in situ irradiation coupled with precession electron diffraction analysis, defect absorption was tracked for increasing dose. Denuded zones were found to collapse, but in the absence of any detected change in macroscopic degrees of freedom of the grain boundaries. Each grain boundary denuded zone experienced changes different doses, indicating a direct observation of the difference in grain boundary “immunity” to irradiation depending on character. Since a change in sink efficiency is likely due to a change in point defect absorption at the boundary, this indicates that something about the structure of these boundaries has changed. The grain boundary macroscopic character remains the same, however, leading to the conclusion that a change in microscopic character has occurred, possibly due to the formation of extrinsic defects in the boundary. To analyze this further, simulations were used to explore grain boundary microstates loaded with defects (mimicking a collision cascade) and assessed for vacancy formation energies. Overall, the results present a foundation for improving sink efficiency descriptions under irradiation, and take a step forward in understanding complex interfacial dependencies. Additionally, results will be shown for studies of grain boundary structure and stability, including facetting, in the context of grain boundaries acting as “phases.” These advances present the possibility that the extent to which a grain boundary’s microscopic degrees of freedom change controls sink efficiency, and thus presents an opportunity to tune such efficiency as the defect scale.

2:00 PM CP04.07.02
Atomicistic Multiscale Modeling of Compositional and Defect Dynamics for Ion Irradiation Synthesis of III-V Semiconductor Quantum Dots
Michael Lively1, Michael Toriyama1, and Jean Paul Allain2,1; Nuclear, Plasma, and Radiological Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Directed irradiation synthesis (DIS) and directed plasma nanosynthesis (DPNS) are robust, scalable approaches to design and fabricate surfaces and interfaces with unique, multi-functional properties at the nanoscale. In particular, DIS/DPNS can be used to rapidly fabricate hexagonal arrays of semiconductor quantum dots at III-V semiconductor surfaces in a single process step [1]. These are desirable for their excellent optoelectronic properties, including sharply-peaked density-of-states and sharp luminescence lines [2]. However, the ion irradiation process introduces significant damage and disorder to the surface, leading to the formation of a nanometers-thick, compositionally-complex amorphous layer at the interface [3], which significantly degrades the optoelectronic properties of the III-V quantum dots. Therefore, a fundamental atomicistic understanding of the irradiation-driven defect dynamics and structural-compositional disorder is crucial for optimized fabrication of these nanostructures.

We have carried out large-scale molecular dynamics (MD) simulations of low-energy (500 eV) Kr++ ion irradiation of GaSb surfaces on the Blue Waters supercomputer at the University of Illinois [4]. These simulations have shown that the irradiation-induced altered compositional depth profile drives phase separation into clusters of the enriched component (Ga or Sb) at a given depth, with characteristic sizes of a few nm, surrounded by 50/50 amorphous GaSb. The nanoscale interface between these clusters and the "bulk-amorphous" 50/50 GaSb are a region of elevated potential energy, which can function as diffusion sinks or as pathways for accelerated transport at the atomic scale. From MD simulations of ion irradiation from the initial (pristine) surface to the structure formation threshold fluence, we observe the formation of small, unstable “protoclusters” of Sb throughout the surface from prompt ion effects. The Sb protoclusters are usually <1 nm in size and contain ~4% of all Sb atoms in the GaSb. However, no evolution of a global compositional gradient emerges from these simulations, indicating that long temporal scale effects such as defect-mediated diffusion are necessary to model the complex compositional evolution of the surface. Analysis of the atomic bonding in the irradiated surface indicates a strong preferential mobility of Sb atoms, suggesting accelerated Sb diffusion to the cluster/bulk interface as the protocluster growth mechanism.

To elucidate the defect dynamics and atomic diffusion mechanisms, we have developed a hybrid MD/KMC model to connect short and long temporal scales in a single simulation framework. The KMC component models atomic diffusion through the disordered layer via a lattice-free method which relies on “in-situ” characterization of the point defects generated by cumulative ion impacts into the GaSb surface. Using this hybrid model, we test the hypothesis that irradiation-enhanced diffusion of Sb atoms towards the Sb protoclusters interfaces provides the growth mechanism to stabilize Sb protoclusters at 2-3 nm diameters. This mechanism connects the prompt ion-induced structural changes and defect production to three-dimensional compositional evolution and surface morphology of III-V surfaces. We study the influence of the surface temperature on the defect dynamics and recovery rates, showing how manipulating the ratio between ion flux and surface temperature during DIS/DPNS processing offers a route towards minimizing damage and optimizing the properties of the resulting III-V quantum dots.


2:15 PM CP04.07.03
Atomic-Scale Mechanisms for Interfacial Radiation Damage Resistance of Oxide Heterostructures
Steven R. Spurgeon, Michel Sassier, Tiffany Kaspar, Weilin Jiang and Vaithiyalingam Shutthanandan; Pacific Northwest National Laboratory, Richland, Washington, United States.

Functional oxide interfaces exhibit useful emergent properties for electronics and sensors, but little work has been done to examine their degradation in high-radiation environments, such as in spacecraft and nuclear reactor cores. While grain boundaries in metals are known to respond much differently than the bulk, less attention has focused on the behavior of engineered oxide interfaces, which offer the potential to finely control structural, chemical, and electronic parameters. Here we examine the damage response of La2TiO4/SrTiO3, and related heterojunctions using a combination of advanced scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and ab initio theory calculations. We observe that the interface can exhibit markedly improved damage resistance to 1 MeV Zr+ ion bombardment, in contrast to the bulk of the film or substrate. We discuss possible atomicistic damage mechanisms and identify unique features of the interface that can influence the damage process. This work suggests that engineered oxide interfaces may offer a means to tune both functional properties and damage resistance, with potential implications for device design in extreme environments.

2:30 PM BREAK
Laser-assisted probe tomography (LAPT) is a powerful tool for materials characterization due to its desirable combination of high spatial resolution and analytical sensitivity. In state of the art LAPT the thermal transient from a near-UV laser (E = 3.5 eV to 3.6 eV; 343 nm to 355 nm) provides the energy to overcome the activation barrier for field ion evaporation. This technique is generally superior to voltage pulsing, which is limited strictly to conductors, and has allowed APT to expand its capability to effectively analyze a wide-range of materials including semiconductors and insulators. However, the thermal process is not without drawbacks. For example, LAPT data quality can be degraded due to thermal tails that limit sensitivity, formation of cluster ions that may have isobaric overlap with elemental species or dissociate into undetected neutral species which can adversely influence composition measurements. This is especially true for many ionic and covalent materials and can limit the recovery of bulk stoichiometry or composition to a narrow range of experimental conditions, if at all [1,2].

Ionizing radiation in the extreme ultraviolet (EUV) region of the electromagnetic spectrum (10 eV to 100 eV; 124 nm to 12 nm) may offer a potential athermal field ionization pathway. Dependent on the particular photon energy used, EUV radiation is above the band gap, work function and ionization potential of any naturally occurring element. Photoionization cross-sections peak in the EUV band across the entire periodic table, and EUV is highly absorbed within the first few nm of the sample surface [3]. Coherent EUV radiation may also offer a potential in situ method for imaging the evolving specimen shape in real time through simultaneous coherent diffraction imaging or related methods [4].

This finding has significant consequences. For example, EUV-APT may be able to measure nanoscale composition measurements in materials systems where the functionality depends critically on an unknown composition or stoichiometry at the local level, or where non-equilibrium phases play a role. This can be as simple as measuring and mapping the variation of a known reaction layer or compound formed during thin film deposition. Another example is in resistance switching oxides that have potential use in non-volatile memory and memristors in neuromorphic computing elements for beyond-CMOS quantum information systems. In these materials, oxygen deficiency (e.g. the oxygen vacancy concentration) plays a critical role in the nanoscale, conductive filaments responsible for the desired functionality. Other applications include hydrogen separation membranes, oxidation catalysts, ion conduction materials, and superconductors.

References:

Sub-Nanoscale Chemistry Across an Abrupt SiO2/Si Interface Using Vibrational Electron Energy-Loss Spectroscopy Kartik Venkatraman1, Barnaby D. Levin1, Katrina March2, Peter Rez2 and Peter Crozier1, 1School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; 2Eyring Materials Center, Arizona State University, Tempe, Arizona, United States; 3Department of Physics, Arizona State University, Tempe, Arizona, United States.

Interfaces are frequently the site of reactions and phenomena that dominate macroscopic properties, even though they are fractionally present relative to the bulk. Widely used vibrational spectroscopies like Raman and Fourier-transform infrared (FTIR) spectroscopy provide chemical fingerprints of bonding arrangements for materials characterization. However, only a few vibrational spectroscopies are effective to probe interfaces at the molecular level, viz. second-harmonic generation spectroscopy and sum-frequency generation spectroscopy. Advances in monochromation in the modern scanning transmission electron microscope (STEM) has made it possible to detect vibrational excitations using electron energy-loss spectroscopy (EELS) [1]. This new capability can be used to investigate the delocalized behavior of bulk as well as the localized behavior of surfaces and interfaces [2]. For a comprehensive understanding of the technique, experiments need to be performed on simple model systems. We explore the spatial variation in different vibrational modes when an electron beam is scanned across an abrupt SiO2/Si interface. This investigation provides baseline data which can be used to further explore the influence of more complex interfaces on vibrational modes in materials.

A 3 μm layer of SiO2 on a Si wafer was prepared for STEM EELS analysis by lifting out a focused ion beam (FIB) lamella using a Nova 200 NanoLab (FEI) FIB. A NION UltraSTEM 100 aberration-corrected electron microscope was operated at 60 kV and equipped with a monochromator that was used to perform EELS linescans across the SiO2/Si interface. The electron interactions in vibrational EELS can be discussed in terms of dipole and impact scattering as done in surface vibrational spectroscopy using high-resolution EELS [3]. The energy-loss spectrum from amorphous SiO2 shows the thin-film bond-stretch mode at 144 meV, a dipole scattering dominated signal, and the bond-stretch plus bend mode at 100 meV, an impact scattering dominated signal. We show that, in practice, the SiO2 thin-film signal at 144 meV is delocalized to ~20 nm and that nanometer resolution is possible when selecting the SiO2/Si interface signal at 136 meV. We also show that the 100 meV vibrational mode in SiO2 was used to measure the interface abruptness to 0.5 nm. Finally, we demonstrate that with vibrational EELS in crystalline Si, which has only impact scattering dominant vibrational modes, a resolution of better than 0.2 nm was achieved with both optical and acoustic phonons [4]. Further experiments on the effect of interfaces such as grain boundaries and twin boundaries on the chemistry in Si will be presented.

References:
[5] The support from National Science Foundation CHE-1508667 and the use of (S)TEM at John M. Cowley Center at Arizona State University is gratefully acknowledged.
conditions to 5% and 20% strain. Using nanobeam scanning diffraction, with a 3nm near parallel-beam probe, we acquired crystallographic information and measured volume fractions of deformation-induced twins and phases within the observed shear bands. We complemented the nanobeam diffraction measurements with atomic-resolution imaging to determine the structure of the interfaces between the martensite phases and the FCC-austenite matrix and to establish the configuration of dislocations at these interfaces. At 5% strain, the non-charged specimens show ample dislocation content from the initial as-forged microstructure with twin-laden shear bands apparent throughout the specimen. In the hydrogen-charged material, dislocation activity is planar at 5% strain, with shear bands containing far less twinning and instead forming ε-martensite. This trend continues up to 20% strain, with non-charged samples only showing general dislocation plasticity and twinning. At 20% strain, hydrogen-charged samples showed large amount of ε-martensite shear bands with α’-martensite within the intersections of the shear bands. Our observations support the strong-breaking notion that ε-martensite is a necessary intermediary in the formation of α’-martensite platelets, as has been described within the classical Olson-Cohen mechanism. However, detailed analysis of the observed structure of the shear-bands raises questions regarding the actual dislocation mechanisms underpinning this transformation. Atomic-resolution observations of an α’-martensite nucleus within an ε-martensite laden shear band shows low dislocation content surrounding the nucleus, indicating that the geometrically contrived distribution of shears of the conventionally invoked Olson-Cohen mechanism for α’-martensite nucleation are inconsistent with the experimentally observed shears. We will discuss alternative interfacial dislocation-based descriptions for the nucleation process and outline potential opportunities and needs for modeling to further clarify the transformation mechanism and its dependence on hydrogen.

**SESSION CP04.09: Solid-Liquid Interfaces**

**Session Chairs: Fadi Abdeljawad and Jeffrey Hoyt**

Thursday Morning, April 25, 2019

PCC West, 100 Level, Room 102 A

### 4:30 PM *CP04.08.04*

**Atomic-Scale Chemical Analysis at Ceramic Interfaces by Advanced Scanning Transmission Electron Microscopy**

Naoya Shibata, The University of Tokyo, Tokyo, Japan.

In recent years, atom-resolved chemical mapping becomes possible by using aberration-corrected scanning transmission electron microscopy (STEM)-energy dispersive X-ray spectroscopy (EDS). STEM-EDS makes it possible to determine almost all the element atoms in periodic table at the same time, so it is advantageous to characterize material interfaces with local chemical inhomogenities. In this study, we applied this technique to understand complex local chemical structures at ceramic interfaces such as yttria stabilized zirconia grain boundaries. By using aberration-corrected STEM combined with high-sensitive silicon drift detectors (SDD), atomic-scale segregation profiles of solute and impurity atoms across ceramic interfaces can be clearly mapped. We demonstrate such chemical analysis elucidates very interesting atomic-scale segregation structures at ceramic interfaces. In this talk, the details of such ultra-high-resolution chemical mapping and new knowledge gained by such observations on ceramic interface segregation will be reported.

### 8:45 AM *CP04.09.02*

**Gallium-Based Liquid Metal Wetting Behavior of Tungsten Powder Facilitated via Electroless Silver Coatings**

Wilson Kong, Matthew Ralphs, Robert Wang and Konrad Rykaczewski, Arizona State University, Tempe, Arizona, United States.

Gallium-based liquid metals are stable liquids at room temperature that exhibit many excellent thermo-physical properties. Liquid metals are useful in applications that require high electrical and thermal conductivity in addition to mechanical deformation. Combining liquid metals with other thermally conductive metallic particles could potentially result in enhancements of these transport properties [1]. However, liquid metals are notorious for alloying with and/or embrittling metals under prolonged exposure due strong intermetallic chemistries. Refractory metals such as tantalum and tungsten are generally resistant to these detrimental processes. However, these metals are unable to directly wet with liquid metals, which prevents them from forming composite fluids. Depositing a thin metallic layer onto these metals can potentially enable refractory metals to be mixed in liquid metal via reactive wetting processes [2]. Electroplating and electroless deposition techniques have long been used to fabricate bi-metallic powders in literature [4]. We show that electroless deposition of silver coatings on tungsten powder can facilitate reactive wetting of these powders in liquid metals. This work demonstrates a relatively simple procedure of forming tungsten-silver core-shell powders and their reactive wetting behavior in liquid GaSn. In-situ focused ion beam (FIB) characterization is utilized for direct observation of this nanoscale wetting process. This work also investigates a time study of potential room temperature alloying processes of the silver layer in a gallium-rich environment under different volumetric fractions of liquid metal/powder. These studies can provide fundamental insights into liquid metal wetting phenomena and how to engineer material surfaces for thermal management, flexible electronics, and plasmonic applications.

References:

### 9:00 AM *CP04.09.03*

**Characterization of Chemically Heterogeneous Metal-Metal Solid-Liquid Interfaces Using Atomistic Simulation**

Brian Laird, Yang Yang, J. Pablo Palacios-Hernandez, Jesse L. Kern and Mark Asta; 1Department of Chemistry, University of Kansas, Lawrence, Kansas, United States; 2Department of Physics, East China Normal University, Shanghai, China; 3Department of Chemistry, College of St. Scholastica, Duluth, Minnesota, United States; 4Department of Chemistry, Randolph College, Lynchburg, Virginia, United States; 5Department of Materials Science and Engineering, University of California, Berkeley, California, United States.

The properties of solid-liquid interfaces (SLIs) govern a wide variety of processes of technological import, e.g., wetting, heterogeneous nucleation, casting, and crystal morphology and growth. Here, we examine three chemically heterogeneous metal-metal SLIs, specifically Al(s)/Pb(l), Cu(s)/Pb(l) and Al(s)/Ga(l) to determine how interfacial structure and dynamics affect phenomena of experimental interest. For Al/Pb, transmission electron microscopy (TEM) experiments show that liquid Pb inclusions undergo Brownian motion within a solid Al matrix. Using molecular-dynamics (MD) simulations, we examine the role played by Al diffusion at the SLI interface in this phenomena and in the spreading of droplets. For Cu/Pb interfaces, earlier simulations predict a strong anisotropy in interfacial structure, with the (100) interface exhibiting surface alloying and the (111) showing a “pre-freezing” region. 2-3 lattice spacings thick, of crystalline Pb at the interface. Using an extensive series of MD simulations we show how this structural anisotropy contributes significantly to differences in the heterogeneous nucleation rates between these two interfaces. Finally, we examine the Al(s)/Ga(l) solid-liquid interface, an important material for the understanding of liquid-metal embrittlement, using both classical and ab-initio molecular-dynamics simulation.
Control of heterogeneous ice nucleation (HIN) is critical for applications that range from iceophobic surfaces to ice-templated materials. Multiple computational studies have been performed to study the effects of the substrate’s surface energy and topography and how their interaction determines phase transition temperature (PTT) and nucleation rates. Two particular well-studied substrates are graphene and silicon. In contrast to a considerable body of literature on computational approaches, few experimental studies have been reported concerning HIN on graphene and the extent of the effect of surface energy on the HIN on plasma-oxidized silicon. The study reported here focuses on the nucleation efficiency of ice on single layer graphene (SLG) deposited on three different substrates: single crystal silicon, fused quartz, and 300 nm SiO₂/Si, as well as plasma-treated silicon with multiple different surface energies. HIN was studied by placing a 1μL water drop on the substrate and observing the PTT using a freezing stage in a Raman spectroscopy system. After each freezing run, the WCA is measured, again. Findings are that the SLG displays surface transparency after only one experiment as indicated by the WCA changing from 95.4°+/−0.4° (a value typical for SLG), to values ranging from 60.9°+/−0.3° to 68.4°+/−0.3°. Such a significant decrease in surface energy was not predicted by computational models suggesting surface topography effects. To investigate the latter, the substrate surfaces were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surprising findings were prominent wrinkles, where the SLG would peel away during the sequential HIN experiments, explaining the change in WCA which occurs due to the lower surface energy substrate being exposed. As a second material system, plasma-oxidized silicon was tested in the same way: as-received, and after 30 s, 120 s, and 300 s plasma exposure with resulting WCA ranging from 32.2°+/−0.3° to −2°. In both systems, the range of observed PTTs was surprisingly small falling within a range from -18.6°+/−0.6°C for the SiO₂/Si substrate (contact angle from 2 to 33 degrees) and -22.5°+/−0.6°C for the graphene substrate (contact angle from 60 to 90 degrees). While the fact that the SLGs were compromised will have contributed to the results obtained for the SLG material systems, the independence from surface energy of the PTT in the case of the plasma-oxidized silicon is an important finding. Both outcomes are noteworthy: 1) The results from the SLG system illustrate the importance of a careful characterization of the substrate before and after nucleation experiments, as it may reveal, as in our case, the suboptimal quality of commercially available SLGs, which poses considerable experimental challenges for the experimental verification of computational results and puts into questions results obtained without such an analysis. 2) The results from the study of plasma-oxidized silicon, which suggest that surface energy or WCA alone are not good indicators of PTT, invite further exploration both experimental and computational.

9:45 AM CP04.09.05
Adsortion Transparency of Supported Graphene to Water Molecules
Morteza H. Baqheri1, Rebecca T. Loibl1, Yingchun Jiang1, Anibal Boscoboinik2, Manuel Smer4,3 and Scott N. Schiffer1,1,1
1,1Mechanical Engineering, Binghamton University, The State University of New York, Binghamton, New York, United States; 1Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 1Material Science and Engineering, Binghamton University, The State University of New York, Binghamton, New York, United States; 1,1Physics, Binghamton University, The State University of New York, Binghamton, New York, United States.

The effect of graphene conformal mapping on the wetting of a surface remains a controversial topic. Many groups have studied the wetting transparency of graphene coated surfaces by measuring the water contact angle on the surface, however, airborne contamination due to the exposure of the surface during contact angle experiment can alter the hydrophilicity/hydrophobicity of the surface. Here, we explore this controversy by comparing the interaction of water molecules with a surface through measurement of the adsorption energy of the water molecules on the surface with and without graphene coatings. Ambient-pressure X-Ray Photoelectron Spectroscopy and quartz crystal microbalance experiments will be reported.

10:00 AM BREAK
Diffusion-induced grain boundary migration (DIGM) - A Molecular Dynamics Simulation

Navjeet Kaur, Chung Deng and Olamrewaju A. Ojo; Department of Mechanical Engineering, University of Manitoba, Winnipeg, Manitoba, Canada.

Diffusion-induced grain boundary motion (DIGM) can be described as normal grain boundary migration phenomenon caused by lateral grain boundary diffusion. In this work, molecular dynamic simulations using Embedded Atom Method potentials and LAMMPS code are performed to investigate the physical origin of DIGM. A comprehensive approach constructed by combining various atomistic simulation techniques, i.e., the synthetic driving force method, the interface random walk method, and shear coupling, has been used to quantify the driving force that operates during DIGM. The driving force obtained from this method is then compared to those arising from coherency strain energy. The two values are consistent with each other, which shows that a key driving force for the phenomenon is that due to unbalanced coherency strain energy across the boundary.

The simulation results also show that segregation plays an important role in promoting DIGM once GB is in close contact with the solute atoms. All observations made during the simulations are supported by the atomistic configurations and graphical analysis at different stages of the process. This phenomenon is of immense technological importance because of its scientific and practical significance in materials.

11:45 AM CP04.10.05

Interface Energy and Orientational Dependence of Interface Velocities and Mobilities of an Austenite-Ferrite Interface in Pure Fe Using Molecular Dynamics Simulation

Pawan K. Tripathi and Somnath Bhownick; Material Science and Engineering, IIT Kanpur, Kanpur, India.

Austenite (γ-Fe, face-centered cubic (FCC)) to ferrite (α-Fe, body-centered cubic (BCC)) phase transformation in steel is of great importance from the point of view of industrial applications. In this work, using classical molecular dynamics (MD) simulations, we study the atomistic mechanisms involved during the transformation of the ferrite phase from an austenite phase. The kinetics of the transformations, classified as martensitic and massive, is defined in terms of the interface mobility, which depends on the interface migration velocity and Gibbs free energy change. The simulations are performed by creating an FCC region, sandwiched between two BCC regions (interface formed according to Nishiya-Wasserman (NW) orientation relationship, with [110] of BCC oriented parallel to [111] of FCC) and studying how the former transforms into the later phase at elevated temperature, ranging from 1000 to 1400 K. Three configurations of BCC-FCC phase were created by tilting FCC phase with respect to z-axis with an angle of 3.11°, 4.04° and 5.77° from the ideal NW, resulting into formation of steps or disconnections at the interface. Using MD simulations, the effect of the tilt on interface velocities, mobilities and activation energy followed by the interface migration mechanism in each of the orientation will be discussed.
a consistent understanding of the \( n_{\alpha} \) directionality and of the final thin film microstructure characterized by a comprehensive structure analysis. The mechanism of LE was studied in situ as a function of time and temperature by Rutherford backscattering spectrometry and Raman spectroscopy. The graphitization occurred simultaneously with the LE and is completed during the applied heating ramp to 700 °C. The temperature resolved measurements allowed the determination of the onset temperatures and transition rates as a function of the annealing temperature and the stacking order. Finally, the activation energy for both LE directions was estimated. In combination with the thermodynamic calculations, this in situ study allows to identify the metal-induced crystallization via wetting and diffusion along grain boundaries, instead of dissolution/precipitation as the responsible mechanism for graphitization of amorphous carbon with layer exchange in contact with Ni. The proposed model can potentially be used to estimate the catalytic transformation of group 14 elements in contact with transition metals.

Financial support by the Helmholtz Excellence Network DCM-MatDNA (ExNet 0028) is gratefully acknowledged.

2:30 PM OPEN DISCUSSION

3:00 PM BREAK

SESSION CP04.12: Oxide Interfaces
Session Chairs: Emmanuelle Marquis and Jason Trelewicz
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 102 A

3:30 PM *CP04.12.01
Oxide Scale Evolution on Ni and Ti Alloys Talaia Barth, Paul Chao, Kathleen Chou, Emmanuelle Marquis and Emmanuelle Marquis; Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Lifetime of structural alloys used in high temperature applications is often limited by their vulnerability to oxidation. To address this issue, different alloying and/or coating strategies have been developed depending on alloy system and application. Alloy chemistries may be tailored so that a slow-growing, passive oxide scale forms on the alloy surface and protects it from further attack by oxidation. The addition of small amounts of dopants can further reduce oxide growth kinetics and enhance scale adherence. While the principles leading to scale growth are generally understood, the mechanistic roles of alloying elements and synergy between alloy and oxide scale are often less clear. High resolution characterization techniques provide a unique opportunity to uncover new insights into the structure and evolution of oxide scales, and ultimately quantify mechanisms of alloy oxidation. Using our experimental observations, we will discuss the mechanisms of scale growth and the contributions of alloying elements during controlled oxidation exposure of model Ni-Cr-Al and Ti alloys.

4:00 PM CP04.12.02
Morphological Stability and Breakdown of Passive Oxide Films Rohit Ramanathan and Peter W. Voorhees; Northwestern University, Evanston, Illinois, United States.

Most models describing the formation of a passive oxide film on a metal are formulated in one-dimension where the principle assumption is that any interfaces in the system are planar. These models fail to describe the interfacial evolution of morphologically complex oxide films because they neglect interfacial energy and curvature, which are important for self-consistently describing morphological evolution for non-planar interfaces. We extend the Point Defect Model for growing oxide films to multiple dimensions and have modified the boundary conditions to include capillary contributions to the defect chemical potentials at the film interfaces. We perform a morphological stability analysis of the 1D steady-state as a first step toward describing the full morphology evolution of the oxide. Our analysis predicts that a localized thinning instability is present at concave regions oxide-solution interface due to anodic dissolution of the oxide. This instability could be the first step of the formation of pitting corrosion. Our results provide insights to the important role that interfacial energy plays in the evolution of the oxide film and suggests that many 1D models may be inapplicable in a broad class of corrosion processes.

4:15 PM CP04.12.03
Ab Initio Prediction of Metastable Phases at Metal/Oxide Heterointerfaces Aakash Kumar1, Amit Sharma2, Eugen Rabkin1 and David Srolovitz3,4; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Technion - Israel Institute of Technology, Haifa, Israel; 3City University of Hong Kong, Hong Kong, Hong Kong.

Heterophase interfaces such as metal/ceramic and ceramic/ceramic interfaces are ubiquitous to a wide range of technological applications, such as the all-solid-state-batteries (ASSB), Cu(In,Ga)Se2 (CIGS) based photovoltaic cells and numerous other solid-state devices. Transport of atoms along these heterophase interfaces may lead to metastable phase formation at the interface. In this work, we report the experimental observation of two such cases a) HCP type Ni(Fe) phase (ground state is fcc structure) and b) FCC Fe (ground state is bcc structure), after the heat treatment of (solid solution) Ni95Fe5/O-Al2O3 and (solid solution) Ni95Fe5/O-Al2O3 respectively. Using ab initio calculations in conjunction with cluster expansion techniques, within the recently formulated meta Generalized Gradient Approximation - SCAN functional, we develop a general model (based upon interface energies) that can be readily applied to establish the conditions under which metastable phases will exist at/near heterophase interfaces, and then predict their minimum and maximum equilibrium thickness under specified conditions. Our experimentally observed thickness of the hcp-Ni(Fe) metastable phase is within the bounds predicted by the model. This implies that the occurrence of stable phases at these heterophase interfaces may not always be as predicted by the equilibrium thermodynamics but in fact is dependent on the interface energies of these heterophase interfaces.

4:30 PM CP04.12.04
Crystallization of Complex Oxides in Proximity of Semiconductor Surfaces with Non-Planar Geometries Divya J. Peakash1,2, Yajin Chen1, Christoph F. Denekel1, Paul G. Evans2 and Francesca Cavallo1,2; 1Center for High Technology Materials, The University of New Mexico, Albuquerque, New Mexico, United States; 2Department of Chemical and Biological Engineering, The University of New Mexico, Albuquerque, New Mexico, United States.

The crystallization of sputter-deposited amorphous strontium titanate (SrTiO3, STO) films is affected by the proximity of free-surfaces and interfaces with other materials. We have crystallized STO films with a thickness of ~12 nm sandwiched between two Si and SiGe-alloy semiconductors in non-planar geometries. The amorphous STO films were obtained by sputtering onto a room-temperature Si-SiGe heterostructure with a built-in stress imbalance. The released STO/Si/SiGe heterostructure rolls into tubes with diameters of a few microns, placing the STO layers in the proximity of two non-planar (or curved) semiconductor surfaces. The effect of the oxide/semiconductor interfaces on the crystallization process is investigated by heating the rolled-up structures to induce crystallization. X-ray diffraction and Raman spectroscopy provide insight on how the proximity of interfaces may determine the balance between nucleation probability and growth of the crystalline phase. Additional effects associated with heating include a restructurization of the amorphous layer and a change in the tube diameter due to changes in the stress distribution within the rolls.

ACKNOWLEDGEMENT: This work was supported by NSF through the University of Wisconsin Materials Research Science and Engineering Center (award No. 1720415).

4:45 PM CP04.12.05
Revealing the Role of Interfacial Stress on the Polarization Stability of Lead-Free Relaxor Ceramics Julia Glum1,2, Yoon Heo3, Matias Acosta1, Pankaj Sharma1, Jan Seidel1 and Manuel Hinterstein1,2; 1Norwegian University of Science and Technology, Trondheim, Norway; 2UNSW Australia, Sydney, New South Wales, Australia; 3Technische Universität Darmstadt, Darmstadt, Germany; 4Karlsruhe Institute of Technology, Karlsruhe, Germany.

The unique properties displayed by canonical relaxor ceramics, such as the electric field induced transformation from a pseudo-cubic relaxor state to a polar ferroelectric state[1], the associated huge strain[2] and the phase transition mediated polarization reversal mechanism[3], make these materials highly interesting objects for fundamental studies as well

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as versatile components for industrial applications. Especially, the achievement of high strains has drawn significant attention, the origin of which is based on the reversibility of the phase transformation between the ferroelectric and the relaxor state [4]. Many relaxor-ferroelectric systems exhibiting high actuating performance are located in the morphotropic phase region leading to the appearance of multiple crystallographic phases even within single grains. Their ability to take on different phases simultaneously and to change the phase ratio to adapt to external stimuli [5], is another important factor contributing to their exceptional electromechanical performance.

Here, we report on the thermal evolution of the different crystallographic phases in a multiphase (Bi1/2Na1/2)TiO3-BaTiO3 relaxor ceramic and the associated development of interfacial stresses. Upon electric field application, this system exhibits an “intrinsic core-shell structure” of a polar minority phase embedded into a polar majority phase. While the majority phase stays stable with increasing temperature up to the transition into the relaxor state, a gradual de-texturization of the minority phase is observed over the whole temperature range. The surface domain structure was found to decay already at significantly lower temperatures than expected from bulk observations. Development of interfacial stresses due to thermal expansion mismatch between majority and minority phases as well as differences in local stress state between surface and bulk are discussed as driving factors of the phase transition dynamics.

Tailoring of interfacial stresses through adaption of phase fractions opens up a pathway to optimize the strain performance of actuators and materials and can become a useful tool for the stabilization of usually metastable crystallographic phases as well as for property tuning in piezoelectrics and multiferrics.

Controlling the micro/nanostructure of thin films would enable us to explicitly tailor their mechanical behavior. Here, we describe a new process to synthesize thin films with precise microstructural control via systematic, in-situ seeding of nanocrystals, and subsequent crystallization of amorphous precursor films. It was found that varying the seed element affects the final phase of the films once annealed, such as NiTi forming an austenite or martensitic phase when seeded with Cr or Ti, respectively. This gives the ability to control grain size, dispersion, and phase composition of thin films. Additionally, crystallization temperatures potentially decrease with the presence of these nanocrystals, reducing precipitate formation and enhancing mechanical properties.

**8:15 AM CP04.13.02**

**Effects of Case Hardening Treatments on the Microstructure and Properties of Stainless Steel 316L**

Xuyang Zhou

Gwénaëlle Proust

D. Retrain

D. Gallietti

M. Chemki

C. Demangeot

School of Civil Engineering, University of Sidney, Sydney, New South Wales, Australia; University of Technology of Troyes, ICD/LASMIS, Troyes, France; EPF, Riosières-prés-Troyes, France; CRITT-MDTS, Charleville-Mézières, France.

Austenitic 316L stainless steel is presently used for orthopaedic implants due to its biocompatibility and high corrosion resistance. One issue, however, with the use of this material in such applications concerns its low wear resistance. Surface properties can be modified through case hardening treatments in order to improve wear resistance and fatigue life as well. In this study two such treatments were applied on stainless steel 316L. The first treatment was Surface Mechanical Attrition Treatment (SMAT) which is a severe plastic deformation (SPD) process that enhances the surface properties and the performances of a material without changing its chemical composition by creating a nanostructured layer on the top surface of the material. The hardness evolutions below the treated surfaces were measured using micro- and nano-indentation and it was shown that at the top surface an increase of 75% in the hardness can be obtained after SMAT. The effect of SMAT can extent deep beneath the treated surface with the creation of a high deformation zone following the nano-grained layer. This high deformation zone contains larger grains where local misorientations are present, and the material in that region is seeing strain hardening as well. Further to SMAT, some specimens underwent a second case hardening treatment, plasma nitriding, to further enhance their surface properties by the diffusion of nitrogen atoms in interstitial positions in the iron lattice creating additional residual strains at the top surface of the material. Using different microstructure characterization techniques, we were able to determine the microstructural evolution of the stainless steel after these different surface treatments and to determine the effects of creating new grain boundaries by SMAT on the nitriding process. The microstructure features investigated here include thickness of the nanocrystalline layer, size of the grains within the nanocrystalline layer and depth of diffusion of the nitrogen atoms within the material. The microstructure changes are here correlated to the improvement in hardness and wear resistance.

**8:45 AM CP04.13.03**

**Interfacial Solute Segregation Behavior in Nanocrystalline Stabilized Alloys**

Xuyang Zhou

Ankit Gupta

Thomas R. Koenig

Garritt J. Tucker

Gregory B. Thompson

Univ of Alabama, Tuscaloosa, Alabama, United States; Colorado School of Mines, Golden, Alabama, United States.

Significant interest has arisen in the use of solutes to provide thermodynamic and/or kinetic stabilization of nanocrystalline grains. Much of this work has primarily focused on their ability to mitigate grain growth under thermal annealing. In this work, we explore both the grain boundary specificity of such segregation under annealing as well as the mechanical responses of these stabilized nanocrystalline grains under mechanical loads. Using Ni(P) as a case study, we demonstrate a cross-correlative precession electron diffraction – atom probe tomography technique where the P solute segregation to specific grain boundaries was quantified. It was found to be relatively homogeneous on high angle grain boundaries, particularly with an increase in annealing temperature. Where variation was noted, the interfacial excess concentrations varied from zero to upwards of tens of atoms/nm². Subsequently, the alloy film was in situ mechanical loaded in a TEM where the granular evolution was characterized. The experimental results are coupled to atomistic simulations to predict the specific boundary segregation behavior as well as simulating how such partitioning is influencing the granular stability under loads in a thermally stabilized nanocrystalline alloy.

**9:00 AM CP04.13.04**

**Thermal Processes and Mechanisms in Sputtered Nanostructures**

Andrea Hodge

Mork Family Department of Chemical Engineering and Materials Science; Aerospace and Mechanical Engineering Department, University of Southern California, Los Angeles, California, United States.

Nanomaterials, nanolayers (NMMs) are of considerable interest due to their high density of interfaces which lead to unique mechanical, chemical, and thermal properties. Additionally, NMM systems have been shown to undergo several microstructural transitions when annealed at elevated temperatures while still retaining nanoscale features. The microstructural evolution of these materials and the nanostructures that develop after annealing are not well understood but can provide insight of active thermal processes and stabilization mechanisms. To further understand the thermal evolution of these materials, several sputtered NMM systems including Mo-Al, Hf-Ti, W-C and Ta-Hf were annealed to critical temperatures determined by DSC. A wide range of characterization techniques including TEM and APT were utilized to examine compositional changes and gain insight into thermally activated events such as layer roughening, solute grain boundary segregation and phase separation.
Oxygen has been known to have a strong hardening effect on titanium alloys, while also inducing serious embrittlement when its concentration exceeds a limited amount. Yet, commercial purity Ti (CP-Ti) doped with a high oxygen content has been produced recently with both high strength and moderate ductility. To explore the mechanism that controls the superior property, we studied the microscopic deformation of the alloy with microstructural observation using electron microscopes after quasi-static and dynamic loading. The effect of loading rates on the deformation behavior, as well as the role of oxygen content, was examined. The high strain rate sensitivity shown in the alloy was carefully investigated and correlated to its microstructure and oxygen content. As well, the effect of oxygen on deformation and fracture modes was studied in relation to the grain size.

**9:45 AM CP04.13.06**

Mesoscale Crystal Plasticity Modeling of Buckling Behavior of Nanoscale Al-Al$_2$Cu Eutectic Alloy Guisen Liu, Shujuan Wang, Amit Misra and Jian Wang; 1Mechanical and Material Engineering, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 2Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Al-Al$_2$Cu eutectic alloy with nano-laminated microstructure exhibit high strength and good plasticity. Due to the significant difference in elastic properties and plastic deformation capability between Al and Al$_2$Cu phases, structural instability occurs in Al$_2$Cu lamellae associated with elastic buckling when a compression stress is applied parallel to the lamellae. Al lamellae plastically deform via dislocations motions. Al-Al$_2$Cu interfaces play strong barriers for blocking dislocation motions in Al lamellae. Thus, elastic buckling in Al$_2$Cu lamellae is constrained by the elastic-plastic deformation of Al lamellae. To understand buckling behavior of nanoscale Al-Al$_2$Cu eutectic alloy, we developed a mesoscale crystal plasticity model and implemented it into finite element analysis. Plastic deformation in Al lamellae is described by the confined layer slip (CLS) mechanism. The critical resolved shear stress for dislocation slip varies with layer thickness, estimated by CLS mechanism. The strain hardening is described by a phenomenological power law. To capture the essential features of confined layer slip in Al lamellae (dislocation loops glide through the layer and depositate at interfaces), plastic deformation in Al lamellae should be the same through the thickness. However, interface constraints will cause different elastic deformation through the thickness of Al lamellae. We thus divided each Al lamella into three voxels that have the same plastic deformation but may develop different elastic deformation. In comparison, we also conducted a traditional CP analysis in which plastic deformation in three voxels through the thickness of the lamella is calculated individually according to phenomenological power law. In these simulations, plasticity in Al$_2$Cu voxels that have the same plastic deformation but may develop different elastic deformation. In these simulations, plasticity in Al$_2$Cu voxels that have the same plastic deformation but may develop different elastic deformation. In these simulations, plasticity in Al$_2$Cu voxels that have the same plastic deformation but may develop different elastic deformation.
1:30 PM CP04.15.01
Twinning in Multiple Principal Element Alloys—Atomistic Simulation Studies
Jun Ding1, Mark Asta2,3, Robert Ritchie2,3, University of California, Berkeley, California, United States; 2Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

High-entropy alloys (HEAs) are an intriguing class of metallic materials due to their unique mechanical behavior. Achieving a detailed understanding of structure-property relationships in these materials has been challenged by the compositional disorder that underlies their unique mechanical behavior. For instance, extensive nanotwinning occurs at room temperature in the medium-entropy CrCoNi alloy, whose combination of strength, ductility and toughness properties approach the best on record. We present results of employing atomistic computer simulations to investigate twinning behavior in the medium-entropy CrCoNi alloys, considering model systems with random substitutional disorder as well as systems with a high degree of local chemical short-range order (SRO). The planar energetics associated with the twinning as well as parameter related to twinability are found to be strongly influenced local chemical SRO. Furthermore, the migration mechanism of twin boundary under deformation have been studied in the CrCoNi alloys with varying SRO.

2:00 PM CP04.15.02
Atomic Level Mechanism for the Formation of Long Period Stacking Order (LPSO) in Magnesium Alloys
Yiqian Chen, Huan Zhao, Blazej Grabowski, Jing Su, Christian Liebscher, Baptiste Gault and Dierk R. Raabe; Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany.

The atomic-level mechanism for long period stacking order (LPSO) in magnesium alloys has been a challenge over the past decade. Here we show that LPSO structure is a result of impeding phase transition pathway from coherent (C) Guinier–Preston zone precipitation to semi-coherent (SC) intermetallic precipitation due to elemental interactions in magnesium alloys. By incorporating first principles calculations and atomic resolution Z-contrast electron microscopy imaging and energy-dispersive spectral (EDX) imaging with the scanning transmission electron microscopy (STEM) for heterophase interfaces in Mg-Zn-Y system, we have demonstrated that C-SC transition is reversed over a certain range of compositions and as a result, the transition from Guinier–Preston zone to LPSO structure is both thermodynamically and kinetically favorable. These results were then combined with atom probe tomography (APT), therefore providing a quantitative analysis of forming different phases and/or structures at the sub-nano scale. This discovery gives a clear picture of how LPSO structure forms at the atomic level and potentially may provide robust information for economical LPSO structured magnesium alloy designs without rare earth elemental additions.

2:15 PM CP04.15.03
On the Different Relaxation Schemes During Generalized Stacking Fault Energy Analysis in Hexagonal Close-Packed Metals—A Case Study of Magnesium
George Voyiadjis1,2, Reza Namakian1; 1Civil and Environmental Engineering, Louisiana State University, Baton Rouge, Louisiana, United States; 2Computational Solid Mechanics Laboratory, Louisiana State University, Baton Rouge, Louisiana, United States.

Generalized stacking fault energy (GSFE) analysis is a valuable technique to provide some insights and information on dislocation core structures and mobilities which are controlled by crystal resistance to shearing along a specific crystallographic plane. This technique is composed of the following steps: 1) cutting a single crystal along a fault plane, 2) shifting rigidly the upper half of the newly created bi-crystal along an arbitrary fault vector which belongs to the fault plane, 3) releasing the shifted crystal on the top of the lower half crystal, 4) relaxing the bi-crystal atoms in the direction perpendicular to the newly generated fault plane. By generating GSFE profile, one should be able to recognize the local minima on the profile correspond to stable stacking faults (SFs).

However, the stability of the SFs should be checked once the atoms are allowed to relax in all directions. This issue could be heightened in metals with hexagonal close-packed (HCP), like magnesium or Mg, due to the unsymmetrical feature of atomic configuration on the two sides of the slip direction. In this work, two relaxation directions are considered, out-of-plane (N-direction) and in-plane (P-direction). N-direction is normal to the slip plane which is [10-11], the first pyramidal or compression twinning plane in HCP metals. P-direction is parallel to the slip plane and perpendicular to the slip direction which is <-1012>. Accordingly, N-direction relaxation (one direction relaxation) and N-P-directions relaxation (two directions relaxation) schemes are used here.

To study the effect of different relaxation schemes on GSFE profile for [10-11]<-1012> system, a sample with 80,000 atoms is constructed in which the height of the sample is large enough to minimize the effect of free surface on the fault plane. Four different empirical potentials, three of which designed by embedded-atom method (EAM) and one with modified EAM (MEAM), available in the literature for Mg are employed in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) to generate GSFE profile as described above with N-direction and N-P-directions relaxations.

We report here that results of N-direction and N-P-directions relaxations both coincide partly along direction, however, N-P-directions relaxation shows significant oscillations in the GSFE profile for all four potentials. This deficiency could be attributed to the following reasons. First, GSFE is a nonphysical projection of crystal slip. Dislocation emission and motion incorporate two energy components: 1) initial elastic deformation and 2) breaking of atomic bonds. While the second term can be assessed by the GSFE, the contribution of elastic deformation is absent from the rigid GSFE model. Second, the traditional way of cutting, shifting, releasing, and finally relaxing the atoms to generate GSFE profile due to the unsymmetrical feature of atomic configuration on the two sides of the slip direction causes a force along the P-direction, which influences not only the value but also the location of the calculated GSFE. Therefore, one may observe the fluctuations in the GSFE profile.

To resolve all the above mentioned issues related to the rigid GSFE profile, nudged elastic band method (NEBM) as a minimum path energy finder (MEP) is employed to find precise values of the saddle points in the GSFE profile. The SFE profile obtained by NEBM alignment shows a completely different energy profile in shape and magnitudes with respect to the rigid GSFE such that the magnitude of the energy barriers are reduced significantly thanks to the incorporation of elastic deformation energy in NEBM and non-straight path of the slip trace obtained by NEBM. Therefore, NEBM can provide more accurate and robust results about SFs compared to GSFE method.

2:30 PM CP04.15.04
The Role of Twin Boundaries on Failure Mechanisms in Nickel-Based Superalloys
Zhongbo Zhang1, Yiqiang Chen1 and Michael Preuss1; 1University of Manchester, Manchester, United Kingdom; 2Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany.

Most polycrystalline Ni-based superalloys used in demanding environments contain a high concentration of annealing twins. In contrast to the concept of grain boundary engineering, where low ζ coincidence-site-lattice boundaries are essential to mitigate the intergranular cracking, coherent ζ twin boundaries (TBSs) in Ni-based superalloys are found to be vulnerable for fatigue crack and hydrogen (H)-induced crack initiation. Despite recent extensive studies, the physical mechanism is still elusive, which hampers the alloy optimisation and performance prediction. Here we use multiscale microstructural characterisations and strain analysis, coupled with density functional theory calculation, to achieve a bottom-up understanding in the role of TBS on failure mechanism of γ"-strengthened Ni-based superalloys. We find that during mechanical loading much earlier dislocation plasticity and pronounced strain localisation happen at TBS, and H-induced cracks nucleate and extend along TBS. Multiscale characterisations, from centimetre scale down to sub-nanoscale, and DFT calculations demonstrate that the abnormal response from TBS originates from the distinctive precipitates formed along the TBS. Our work not only uncovers the mechanistic origin of TBS-related failure but also provides a practical method to alleviate the adverse effect of TBS on the performance of Ni-based superalloys in aggressive environments.

2:45 PM CP04.15.05
Preferential Intergranular Corrosion Along Coherent Twin Boundaries in Pure Ni
Mengping Liu1, Matteo Seita2 and Michael Demkowicz2; 1Materials Science and Engineering, Texas A&M University, College Station, Texas, United States; 2Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, Singapore.
We describe an investigation of intergranular corrosion on the surface of pure Ni after cathodic charging. The intergranular corrosion takes the form of long trenches along coherent twin boundaries (CTBs). These trenches are formed by the growth and eventual overlap of conical cavities along <110>-type directions within the CTB planes. We propose that the corrosion cavities initiate at high energy, symmetric incoherent facets along CTBs and deepen due to their local anodic polarization relative to the sample surface. Our observations show that cathodic protection is not guaranteed to prevent corrosion. They also reveal that—for being corrosion resistant—CTBs are especially susceptible to localized corrosion under some conditions.

3:00 PM BREAK

SESSION CP04.16: Property Control Through Grain Boundary Segregation
Session Chairs: William Bowman and Julie Cairney
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 121 B

3:30 PM *CP04.16.01
Nano-Scale Effects on Grain Growth—Grain Boundary Energy and Velocity in Magnesium Aluminate Ricardo H. Castro and Derek N. Muche; University of California, Davis, Davis, California, United States.

Grain boundary mobility is affected by thermodynamic driving force and local velocity of atomic movement. It has been a long-time challenge to separate each individual contribution as they are intimately connect, but such understanding could help provide more reliable strategies for coarsening inhibition in nanocrystalline materials. Here we experimentally demonstrate the individual contribution of kinetics and thermodynamics in magnesium aluminate grain growth, in particular highlighting the nano-scale effects. Fully dense nanocrystalline MgAl2O4 grain growth was studied at different temperatures and a mobility shift - i.e. from a high mobility at small grains to lower mobility for larger grains - was observed below a critical nano-scaled grain size. By combining experimental grain boundary energies and kinetic analyses, we showed that the excess energies associated with grain boundaries at the nanoscale are increased due to the spinel inversion parameters, but there is also a change in grain boundary velocity, likely attributed to a complexion transition associated with the segregation of aluminum to grain boundaries.

4:00 PM CP04.16.02
Enhancing Grain Boundary Ionic Conductivity in Ceramics via Local Solute Enrichment and a New Data-Driven Interacting-Defect Model Describing Nanoscopic Interface Compositions William J. Bowman1, Xiaorui Tong2, David Mebane3 and Peter Crozier4; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, United States; 3School for the Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States.

High ionic conductivity is desired to optimize electrolyte performance, though it is significantly degraded by grain boundaries (GBs), which act as ionically-resisting block layers in polycrystalline electrolytes. Given the rich diversity in GB types, and the complex interplay between structure, composition, and chemistry at the atomic and nanoscale [1-3], there is considerable opportunity to elucidate fundamental science and performance optimization of GBs. Hence, studies should rely on GB datasets correlated across many length scales, with the aim of generalizing high spatial resolution observations to an entire GB population. This should facilitate bottom-up design of GBs with optimized properties, which remains a considerable challenge. By combining suitable modeling approaches with experimental measurements interrogating materials over different length scales, it becomes possible to estimate the electrical properties of individual GBs.

Here, we show that the enhancement of oxygen ionic conductivity by over two orders of magnitude in an electroceramic oxide is explicitly shown to result from nanoscale enrichment of a grain boundary layer or complexion with high solute concentration. A series of Ca1−xCexO2−δ polycrystalline oxides with fluoride structure and varying nominal Ca2++ solute concentration elucidates how local grain boundary composition, rather than structural grain boundary character, primarily regulates ionic conductivity. A correlation between high grain boundary solute concentration above ~40 mol6%, and four orders of magnitude increase in grain boundary conductivity is explicitly shown. A correlated experimental approach provides unique insights into fundamental grain boundary science, and highlights how novel aspects of nanoscale grain boundary design may be employed to control ion transport properties in electroceramics.

Additionally, we present a new data-driven interacting-defect model that has quantitatively described the nanoscopic composition of high solute concentrations at grain boundaries in ion-conducting ceramics. The successful model is a Cahn-Hilliard methodology for interfaces, introduced and demonstrated in this report. The model is applied to high spatial resolution composition data gathered at grain boundaries in calcium-doped ceria. The statistical methodology for the data-driven procedure shows definitively that gradient terms are required to model defect interactions to quantitatively describe the local grain boundary composition data. The model additionally predicts co-aggregation of negatively-charged acceptor dopants and positively-charged oxygen vacancies at the interface, which is in accordance with atom probe tomography in acceptor-doped ceria.

Acknowledgements
NSF Graduate Research Fellowship (DGE-1211230), NSF grant DMR-1308085, ASU’s John M. Cowley Center for High Resolution Electron Microscopy.

References

4:15 PM CP04.16.03
Atomistic Studies of Effects of Alloying Element Segregation on Grain Boundary Cohesive Strength in Fe-Based Alloys Axel E. Alcocer Seoane and Xiao-Ming Bai; Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States.

Fe-based alloys are important structural materials for many engineering applications. Segregation of alloying elements and impurities to grain boundaries (GBs), either due to radiation induced segregation (RIS) or thermal segregation, can alter the GB cohesive strength and thus affect the fracture resistance of these alloys. Therefore, it is important to understand how the segregation of different alloying elements and impurities influences the GB cohesive strength. In this work, we use molecular dynamics simulations to study the changes of GB cohesive strength due to the substitutional segregation of P, Al, V, W, Cu, Ni and Cr at $\Sigma 3^{<111>}$, $\Sigma 3^{<112>}$, $\Sigma 5^{<012>}$ and $\Sigma 5^{<013>}$ GBs in body centered cubic (bcc) Fe. It is found that V, W increase the GB cohesive strength while P, Cu reduce it and Al, Cr, Ni have small effects. Additionally it is found that $\Sigma 3^{<111>}$ GB is influenced the most by segregation and the alteration in GB cohesive strength is correlated to substitution energy in the bulk.

4:30 PM CP04.16.04
First-Principles Studies of Effects of Oxygen Impurity on Grain Boundary Strength in Nickel Zisi Xiao and Xiao-Ming Bai; Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, United States.

Grain boundary (GB) is one of the most important microstructures that govern the physical properties of materials. In many metallic systems such as nickel-based alloys, GBs are susceptible to intergranular fracture and stress corrosion cracking. Using first-principles calculations, we have investigated the strength of $\Sigma 5^{(012)}$ and $\Sigma 3^{(111)}$ GBs with different oxygen concentrations in both substitution and interstitial sites. As expected, our results show that oxygen is an embrittling element at both two sites. For each case, we compare the energy difference between mechanical distortion effect and chemical bond influence. Electronic analyses such as density of states (DOS) and charge density distribution are conducted to study the role of chemical bonds on GB strength.
Ceramic oxides are used for a wide variety of technologically relevant applications from electrochemical devices, novel resistive switching devices and oxygen sensors. Applications such as these typically rely upon the ability of oxides to conduct ions efficiently through the lattice. For oxides, such as CeO$_2$ (ceria), it is common to dope with aliovalent elements to increase the number of available charge carriers. While bulk-doping methods developed to optimize ionic conduction in the bulk have been successful, they have provided little insight when optimizing the grain boundary (GB) conductivity in these polycrystalline oxides. Unlike the bulk, GBs are often subject to complex segregation behavior, structural disorder, space charge effects as well as the standard defect-defect interactions typically present in the bulk. Recent nanoscale compositional characterization has shown different nominal concentrations could result in orders of magnitude increase in GB ionic conductivity relative to the undoped samples [1]. This effect has been attributed to increases in local dopant/solute concentrations at the GB. This study aims to understand how high concentrations of dopants, namely Ca, present at the GB increases the ionic conductivity.

To understand the key factors influencing the ionic conductivity, computational modeling is employed using molecular statics to optimize the GB interfacial structure for three the ionic conductivity.

In order to capture the changes in conductivity for various GB models, Migration energies, local strain and various oxygen migration pathways across each GB are compared to elucidate the role of local composition in modulating oxygen migration across GBs. Energetics and structural stability trends obtained using molecular statics/dynamics are validated using density functional theory calculations. This study further develops our understanding of the interplay between nanoscale composition and structure with high dopant concentrations enabling the development of methods such as selective doping to improve macroscopic ionic conductivity for both the grain and GB.

[2] We gratefully acknowledge ASU’s HPC staff for support and assistance with computing resources, NSF grant DMR-1308085, and ASU’s John M. Cowley Center for High Resolution Electron Microscopy.

**SYMPOSIUM CP05**

**Materials Evolution in Dry Friction—Microstructural, Chemical and Environmental Effects**

April 23 - April 25, 2019

**Symposium Organizers**

Koshi Adachi, Tohoku University

Christian Greiner, Karlsruhe Institute of Technology

Judith Harrison, United States Naval Academy

Michael Moseler, Fraunhofer Inst

**Symposium Support**

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* Invited Paper

**SESSION CP05.01: In Situ Observation of Materials in Nanoscale Tribology**

Session Chairs: Koshi Adachi and Michael Moseler

Tuesday Morning, April 23, 2019

PCC West, 100 Level, Room 102 B

**10:30 AM *CP05.01.01 In Situ Observations of Nanotribology Evolution Laurence Marks:** Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States.

An important, and also sometimes controversial issue in nanotribology is how does a microstructure evolve? Is it purely stochastic, or are there some systematics underlying the science which occur naturally and/or can be exploited to reduce friction and wear. Over the last decade there has been a slow increase in the use of in-situ sliding within transmission electron microscopes. While these instruments normally are less sophisticated than dedicated scanning probe instruments or aberration-corrected microscopes, by combing the two one can obtain information about what matters, what does not which is often obscured by the buried interface in less direct experiments. This talk will focus on some older and some new results from in-situ observations inside electron microscopes. We find that the evolution is not purely stochastic, but instead involves fracture of weak links and the reduction of high friction local structures.

**11:00 AM *CP05.01.02 Atomic-Scale Insights into Contacts Between Nanoscale Bodies—In Situ Experiments and Matched Atomicistic Simulations Tevis D. Jacobs,* Sai Bharadwaj Vishnubhotla, Subarna R. Khanal, Rimei Chen, Xiaoli Hu and Ashlie Martini; Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; *University of California, Merced, Merced, California, United States.**

In probe-based microscopy, nanomanufacturing, and small-scale devices, the performance and reliability often depend on the size and nature of contacts between nanoscale bodies. However, conventional models of contact based on continuum mechanics rely on assumptions that may not hold at the nanometer length scale. Here we used a combination of in situ experiments and atomistic simulations to quantitatively investigate nanoscale asperities during formation, loading, and separation of contact. Experimentally, contact tests were performed inside of a transmission electron microscope, with in situ measurements of load and contact properties taken simultaneously with high-resolution characterization of the materials structure and geometry. In simulations, molecular dynamics modeling was performed on identical nanocontacts that were precisely matched in terms of materials, geometry, and loading conditions. The results demonstrate that important contact properties such as adhesion, contact size, and electrical current flow deviate significantly from the predictions of conventional models. The physical origin of the deviations is shown to be chemical and mechanical interactions at the atomic scale.

**11:30 AM CP05.01.03 Micro-Mechanical Investigation of Microstructure Effects on Dry Friction Gianluca Roscioli and C. Cem Tasan; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.**

In absence of physically-based constitutive relations describing mechanisms of abrasive wear, design of wear-resistant materials has been driven either by (i) trial-and-error based alloy screening approaches, or (ii) following the Archard equation that linearly relates wear resistance to the hardness of the annealed material. There are, however, observations in literature that demonstrate that hardness is not the only factor controlling abrasive wear response. In an effort to unravel the key constitutive relations, a systematic study on the role of crystal structure and orientation has been performed. Grains with specific orientations of IF steel and pure nickel, heat treated to obtain similar micro-hardness values, have
been selected using EBSD to perform in-situ SEM scratch tests with the same applied force. Focused Ion Beam has been used in order to confirm that the dry friction tests were conducted in ploughing mode, and Atomic Force Microscopy as a way to quantify wear from the surface profile. Comparing the results for the two different crystal structures and for grains with different crystal orientations enabled the identification of guidelines for design of advanced wear-resistant materials.

11:45 AM CP05.01.04
In Situ Atomic-Scale Observation on Friction Between Metallic Contacts Scott X. Mao1, Yang He2 and Chongmin N. Wang2; 1University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 2Pacific Northwest National Laboratory, Richland, Washington, United States.

Atomic friction is imperative to the performances and reliability of micro-/nano-electromechanical systems and magnetic storage devices. Nevertheless, the atomic mechanisms underlying friction are still elusive, primarily due to a lack of direct observation on the contacting interface during the process. Here, by combining in situ atomic-scale transmission electron microscopy (TEM) and atomic force microscopy (AFM), we discovered diffusion-mediated formation of an interfacial layer between two metallic asperities under trivial normal forces, which was responsible for ultra-low friction. In addition, the atomic friction mechanism was found to depend on the mutual orientation of the contacted crystals. The work demonstrates fundamental insights and a new avenue for atomic friction.

SESSION CP05.02: Tribology of 2D Materials
Session Chairs: Martin Dienwiebel and Laurence Marks
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 102 B

1:30 PM CP05.02.01
Fundamental Insights into Dry Friction, Adhesion and Wear via Nanoscale and In Situ Approaches Robert Carpick; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

New insights into friction and lubrication from atomic force microscopy (AFM) are presented. First, nanocontacts with 2-dimensional materials including graphene and MoS2 are discussed. Friction between nanoscale tips and 2D materials has been repeatedly shown to depend on the number of layers. An initial model attributing this to puckering [1] is now enhanced by molecular dynamics (MD) simulations showing a strong role of energy barriers due to interfacial pinning and commensurability [2]. New results where 2D materials are used on both the tip and the sample will also be presented. Then, nanoscale asperity-on-asperity sliding experiments conducted using a nanoindentation apparatus inside a transmission electron microscope will be discussed. This experiment is used to obtain atomic-scale resolution of contact formation, sliding, and adhesive separation of two silicon nanosuperlattices. Forming and separating the contacts without sliding revealed small adhesion forces; separating during sliding resulted in a nearly 20 times increase. These effects were repeatable multiple times, and increased with both the sliding speed and the applied load used. We attribute this surprising sliding-dependent adhesion to the removal of passivating terminal species (likely hydrogen atoms) from the surfaces, followed by re-adsorption of these species after separating the surfaces. This helps explain mechanisms of nanoscale dry adhesion, and demonstrates that adhesion can be reversibly varied, which offers potential applications for nanoscale manipulation.


2:00 PM CP05.02.02
Atomic Origins of Temperature-Dependent Shear Strength in 2D Materials Adam R. Hinkle1, John Curry1, Tomas Babuska1, Michael T. Dugger1, Brandon A. Krick2, Nicolas Argibay2 and Michael Chandross3; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Lehigh University, Bethlehem, Pennsylvania, United States.

We present a model that predicts the macroscale temperature-dependent interface shear strength of 2D materials like MoS2 based on atomistic mechanisms and energetic barriers to sliding. Atomic simulations were used to systematically determine the lamellar size-dependent rotation and translation energy barriers, that were used to accurately predict a broad range of experimental data. This framework provides insight about the origins of characteristic shear strengths of 2D materials.

2:15 PM CP05.02.03
Temperature and Speed Dependence of Nanoscale Friction for Mono- and Multilayer MoS2—A Combined Atomic Force Microscopy and Molecular Dynamics Study Kathryn Hasz1, Mohammad R. Vaziriserehsk2, Ashlie Martini2 and Robert Carpick1; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2University of California, Merced, Merced, California, United States.

There has been a sustained interest in 2D and layered materials for use as solid lubricants due to their intrinsically low friction, and in advanced electronics applications including flexible electronics due to their intrinsic bendability and novel electronic properties. It is known that both temperature and sliding speed affect friction, but there is little understanding about the relative importance of these effects. We use matched ultrahigh vacuum atomic force microscopy (AFM) experiments and molecular dynamics (MD) simulations to study the atomic stick slip friction for nanoscale SiNx and Si tips sliding on monolayer and multilayer MoS2 from cryogenic to elevated temperatures, and over several decades of sliding speed. We observe that friction increases as temperature decreases and as speed increase. In agreement with the qualitative trends predicted by the thermal Prandtl-Tomlinson model, friction shows an approximately logarithmic increase with increasing sliding speed. In some cases, we observe dramatically decreases in friction as temperature increases, suggesting the effective role of thermolubricity. Similar trends are seen for monolayer and multilayer MoS2. However, the temperature dependence differs between different tip materials, potentially due to the difference in thermal conductivity of the tip and across the tip-sample interface. These new findings have important implications for macroscale and nanoscale solid lubrication, and for applications using layered and 2D materials including the assembly and functionality of flexible electronics.

2:30 PM CP05.02.04
Environmental Contamination Affecting Friction in Graphene Clara Almeida1, Felipe Ptk2 and Rodrigo P. Menezes2; 1Unimetro, Duque de Caxias, Brazil; 2Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil.

Environmental contaminations are known to affect the use of nanoscale materials in devices. In this contribution, we show that friction in graphene is significantly altered by the presence of contamination that comes from air exposure. The influence of contamination in tribological properties was studied by friction force microscopy. It was observed that friction in graphene increases due to surface contamination, decreasing the difference in friction between mono and bilayer graphene. The physisorption of contaminants was observed to begin at the edges or mechanical defects in graphene monolayers. Time series of friction force images enable us to observe the kinetics of this contamination spreading over the surface.

2:45 PM CP05.02.05
Sliding Over 10,000 Times Faster—QCM Integrated Microtribometry to Probe Friction Fundamentals via Gold and Single-Crystal MoS2 Nikolay T. Garabedian1, Raymond Wieser2, Gabriel McAndrews2; 1University of Delaware, Newark, Delaware, United States; 2Physics, St. Olaf College, Northfield, Minnesota, United States.

A major focus of tribology research has been to understand the origins of practical-scale multi-asperity friction by dissecting it down to nano-scale single-asperity contacts. The Prandtl-Tomlinson model with thermal activation (PTT) has laid the theoretical foundations for understanding friction of single-asperity contacts. Experimentally, both molecular dynamics and friction force microscopy have agreed with PTT model’s prediction that friction increases logarithmically with velocity. Multi-asperity contacts’ velocity dependence, on the other hand, is much more challenging to describe theoretically and verify experimentally. In this presentation, we show an experimental setup that consists of a microtribometer that simultaneously uses two lateral motion devices with vastly different characteristic velocities: a piezo stage (<0.1 mm/s) and a quartz crystal microbalance (QCM) (up to 1 m/s). We also have two independent opportunities to measure the frictional responses of the contact: using either the capacitance sensor-based microtribometer
Fundamental Links Between Microstructure, Environment and Friction in Metals

understanding of the fundamental aspects of how shear stress may affect the microstructure and chemistry of PFA. The objective of this work is to link the chemical and physical aspects of fracture mechanics, which includes the tribological behavior of the polymer composite and the mechanical properties of the fillers.

Dry friction is commonly desired in extreme environments where traditional lubrication solutions such as oils and greases are precluded. Polytetrafluoroethylene is an excellent candidate material for dry sliding applications due to its low friction coefficient, high resistance to chemical attack, vacuum compatibility, and wide range of operating temperatures. Although it suffers from a notoriously high wear rate, k~7 x 10^-4 mm^3/(Nm), filler materials from microparticles to fibers provide modest to moderate improvements in wear resistance, typically by one to two orders of magnitude. The formation of a stable transfer film is largely believed to be a critical step towards attaining ultralow wear in sliding against metal counterfaces; however, the specific tribomechanical mechanisms of transfer film formation have only very recently been investigated. In this study, a “striping” experiment permitted spectroscopic analyses of PTFE/alumina transfer films in various stages of development. This study led to a proposed mechanism that details the formation of chemically-distinct films on both surfaces of the tribological pair. PTFE chains break due to the mechanical stresses generated during sliding and, in the presence of oxygen and water in the ambient environment, produce carboxylic acid end groups, which chelate to both the surface of the alumina filler and the exposed metal counterface and nucleate the formation of the transfer film. These tribomechanical reactions form a thin and robust polymer-on-polymer tribological system that after the initial run-in period can endure hundreds of thousands of reciprocating sliding cycles with virtually no polymer composite wear. The Hamaker model for van der Waals interactions between polymer fibrils and the countersurface provides mathematical support for the mechanical scission of carbon–carbon bonds in the backbone of PTFE under sliding contact conditions. Model experiments utilizing small molecules have confirmed the proposed reactions.

INTRODUCTION: Though it has similar mechanical, thermal, and chemical properties as polytetrafluoroethylene (PTFE), perfluoroalkoxy polymer (PFA) has rarely been evaluated in tribological (friction and wear) applications. In addition to its unique physical, thermal, and chemical properties, PFA can be melt-processed instead of the sintering-based methods of PTFE. This allows filler particles or fibers to be melt mixed with PFA and this mixture can be used to produce complex geometries via screw-injection molding. The wear rate of PFA was shown to improve nearly four orders of magnitude with the addition of 5-10 wt. % of α-alumina filler particles, highlighting the need for a better understanding of the fundamental aspects of how shear stress may affect the microstructure and chemistry of PFA. The objective of this work is to link the chemical and microstructural observations of unfilled PFA the observations seen in PTFE-alumina and PFA-alumina composite systems.

METHODS: Differential scanning calorimetry (DSC), x-ray diffraction (XRD), transmission infrared spectroscopy, and attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) were used on bulk and worn samples of unfilled PFA and PFA-alumina composites were slid against stainless steel counterfaces at 6.25 MPa of applied pressure and a sliding velocity of 50 mm/s.

RESULTS & DISCUSSION: Tribological experiments revealed a 10,000x improvement in wear of PFA-alumina composites (K~4.0x10^-4 mm^3/(Nm)) compared to unfilled PFA (K~4.0x10^-2 mm^3/Nm)). Additionally, PFA-alumina composites were found to have similar friction (μ~0.25) which is surprising considering unfilled PFA (μ~0.12 has a friction coefficient nearly 2x lower than that of unfilled PFA (μ~0.24). Wear properties of PTFE-alumina composites (K~4.4x10^-4 mm^3/Nm) matched those observed in filled PTFE composites. The reduction in wear rate for PTFE-alumina and PFA-alumina composites has been attributed to tribochemical reactions of broken fluoropolymer chains, environmental constituents, and the metallic countersurface/aluminum oxide filler material. These reactions promote the development of running films and transfer films that protect the surface of the polymer composite and steel counterface.

To better understand this tribomechanical mechanism, tribological experiments of PFA compared to PTFE, the effects of sliding on the microstructure and chemical makeup of PFA were investigated. From observations of DSC endotherms, PFA wear debris had higher crystallinity compared to bulk PFA. Additionally, XRD of unworn and worn PFA showed an increase in crystallite size for the wear debris. Both these observations point to microstructural rearrangement of the PFA backbone due to stress applied during sliding, which have also been reported in the wear of unfilled PTFE and drawing of PTFE films. Higher concentrations of PAVE comonomer were seen in ATR-IR spectra of PFA wear debris, suggesting preferential crack propagation through the amorphous region of the microstructure of PFA during sliding. Similar repeated loading during MIT flex life experiments on PFA showed that PFA samples with lower crystallinity of PFA (higher % amorphous region) exhibited improved fatigue performance, suggesting that cracks preferentially travel through the amorphous region of PFA. Transmission IR spectra of PFA wear debris revealed the presence of free carboxylic acid endgroups that were not present in the bulk PFA surface. The presence of free carboxylic acids is due to the breaking of C-C bonds in the PFA backbone reacting with environment constituents. The formation of free-carboxylic acids endgroups is a critical intermediate step of the tribochemical reaction necessary to form robust transfer films and running films proposed for PTFE-alumina composites.
Are Tribofilm Properties Predictive of Wear Resistance?

In tribological systems, wear is a dynamic process that leads to adhesive transfer, material mixing, and oxidation. All of these phenomena, along with the mechanical deformation of the near-surface, lead to the formation of tribofilms, which are also called mechanically mixed layers. Microstructural and chemical modification of tribofilms lead to enhanced frictional behavior and wear resistance.

During sliding of surfaces, the near-surface undergoes significant changes in terms of topography, composition, and microstructure. These changes affect the wear properties of materials. The study of tribofilms is crucial for understanding wear mechanisms and developing materials with improved wear resistance.

The role of shear deformation on generating tribofilms is a topic of ongoing research. Shear force applied to metallic materials can induce deformation and microstructural changes which can be used to process materials in solid state, helping avoid melt processing and in achieving highly refined microstructures not achievable by conventional processing. In order to develop such solid phase processing methods for metallic alloys, we aim to better understand the fundamental atomic scale mechanisms of mass and energy transfer in materials under shear deformation. Formation of metastable interfacial states in metallic multilayer thin film systems with different miscibility between individual layers under shear deformation, unique deformation mechanisms and accelerated diffusion observed only under high shear deformation are crucial factors to be understood. We employ a pin-on-disk tribometer deformation of various thin film stacks based on Cu and Al systems followed by detailed microstructural characterization before and after shear deformation by transmission electron microscopy, atomic force microscopy and atom probe tomography to understand the structural and compositional changes near atomic scale resolution. Our results on structural and chemical modifications at interfaces and individual layers of thin films after shear deformation versus thermal annealing provide new insights on the unique role of shear deformation on modifying the phase transformation pathways of these alloy systems. These new insights will be presented and compared with what is currently understood about role of shear deformation on generating super saturated solid solution states or self-organized nanolayers in immiscible metallic alloys.

8:45 AM *CP05.04.02 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys Martin Dierschiel, 3, 4 and Ebru Cihan; 1 Microtribology Center μTC, Institute for Applied Materials IAM-CMS, Karlsruhe Institute of Technology, Karlsruhe, Germany; 3Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany.

9:15 AM CP05.04.03 Shear Deformation Induced Intermingling and Structural Modifications of Metallic Multilayer Thin Films Arun Devaraj, 1, Aashish Rohatgi, 2, Peter V. Suzalco, 1, Sreen N. Mathadu, 3 and Cynthia Powell, 3 Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States; 3Department of Materials Science and Engineering, Mechanical Engineering, University of California, Riverside, Riverside, California, United States; 4Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States.

9:30 AM CP05.04.04 Microstructure Evaluation of Nanostructured Multilayer Ductile Cast Iron Under Dry Sliding Condition Kewen Dong, Wentao Zhou and Cheng Liu; Yangzhou University, Yangzhou, China.

Ductile cast iron (DCI) is becoming an increasingly important engineering material due to its remarkable strength, ductility, wear resistance and low production cost. However, the industrial heavy-loading components like gears and bearings require improved wear resistance with the wide application of DCIs. An investigation is carried out to examine the influence of austempering time on microstructures and tribological performance of a novel DCI under dry sliding conditions. A commercial unalloyed DCI is used to be austenitised at 900°C for 30min, then rapidly quenched into a patented water-based liquid at 200°C for a very short time, and isothermally held at 190°C (slightly lower than the starting temperature of martensite formation of DCI matrix) for 5, 30, 120, 600 or 720min. It is shown from the tribological test that the superior wear resistance with a minimum mass loss and a lower wear rate can be achieved at 190°C for 120min, which is mainly due to the multiphase synergy between prior martensite (PM), bainitic ferrite (BF), retained austenite (RA) and a unique nano-structure composed of nano-scaled BF and RA enriched with high carbon content (BF+RA)mono, during dry sliding conditions. Particularly, the region with (BF+RA)mono and a certain content RA, exhibits even a higher hardness after dry sliding. Because the normal force engaging during tribological test can induce the martensite transformation locally and give the structure a hard surface layer. The result shows a reasonable value of tribological performance which recommends the designed nanostructured multiphase DCI for more extensive application prospects.

9:45 AM CP05.04.05 Shear Melting of Silicon and Diamond and the Disappearance of the Polymorphic Transition Under Shear Giannietro Morosi, 1 Andreas Klemenz, 1 Thomas Reichenbach, 1 Adrien Gola, 2 Hiroshi Uetsuka, 3 Michael Moseler, 4 and Lars Pasteck, 1, 2 Fraunhofer IWM, MicroTribology Center μTC, Freiburg, Germany; 3Department of Microsystems Engineering, University of Freiburg, Freiburg, Germany; 4Asahi Diamond Industrial Co. Ltd., Chiba, Japan; 5Institute of Physics, University of Freiburg, Freiburg, Germany.

Molecular dynamics simulations of diamond-cubic silicon and carbon under combined shear and compression show the formation of an amorphous solid with liquidlike structure at room temperature. Consistent with the opposite density changes of the two crystals upon melting, the amorphous material is denser than the crystal in silicon and less dense than the crystal in carbon. As a result, its rate of formation is enhanced by pressure in silicon but suppressed in carbon. These results are particularly unexpected for silicon, whose amorphous structure is supposed to be liquidlike (high-density amorphous Si, HDA-Si) only when hydrostatically compressed above the polymorphic transition pressure (~ 14 GPa). Below this pressure, amorphous silicon is expected to have a low-density structure (LDA-Si) with density close to that of the diamond-cubic crystal. Our simulations show that this polymorphic transition disappears under shear and high-density, liquidlike amorphous silicon with metallic ductility forms even at low pressure. These results are potentially transferable to other diamond-cubic crystals, such as germanium and ice Ih, and provide insights into nonequilibrium materials transformations that govern friction and wear in tribological systems.

10:00 AM BREAK

10:30 AM *CP05.04.06 Are Tribofilms Properties Predictive of Wear Resistance? Richard Chronik; Materials Engineering, McGill University, Montreal, Quebec, Canada.

Wear of metals in dry sliding contacts is a dynamic process that leads to adhesive transfer, material mixing and oxidation. All of these phenomena, along with the mechanical deformation of the near-surface, lead to the formation of tribofilms, which are also called microscopically mixed layers. Microstructural and chemical modification of tribofilms lead to significantly different properties from the bulk material that is subjected to dry sliding wear. In some instances, tribofilms can be stable and resist wear and in other cases, there can be persistent wear flow related to tribofilm instability.

Recent advances in nanomechanical testing have made it possible to study mechanical properties of small volumes of materials. Tribofilms present an interesting and challenging vista for nanomechanical testing. In recent years, researchers have used nanoinindentation and pillar compression testing to determine the properties of tribofilms. While a limited number of studies of this type exist, and measurements are difficult to quantify, there is clearly a trend with tribofilms and the wear resistance of a metals and metal-matrix composites (MMCs). In this study, nanoindentation testing of tribofilms revealed that for a wide range of metals (Al, Cu, Ti, Ni) and their MMCs (Al-Al2O3, Ti-TiC, Cu-MoS2 and Ni-WC) that there is a trend of decreasing wear rate with tribofilms hardness. Metals and MMCs are tested in sliding wear and sometimes fretting wear test conditions. For all cases, post-characterization of cross-sectioned wear scars reveals microstructural evolution near surface leading to formation of tribofilms that provide wear resistance and friction control. Structure and properties of the tribofilms are determined with SEM, TEM, EDS, Raman spectroscopy and nanoindentation. Generally, tribofilms are found to be mixtures of the two components in the MMC, but with finer microstructure and some level of oxidation that leads to higher hardness. Using a wider range of test conditions
(e.g. sliding speed, normal load), one can establish additional relationships between tribofilm properties and wear resistance. Furthermore, using recently developed techniques for toughness measurements using nanomechanical methods, a better picture of the overall mechanical properties required for tribofilm stability and wear resistance can be established.

11:00 AM CP05.04.07
Chemical and Microstructural Evolution of Mechanical Contacts by Multiscale Simulations
Izabela Szlufarska, Zhuohan Li and Hubin Luo; University of Wisconsin, Madison, Wisconsin, United States.

One of the critical challenges in designing materials with superior tribological properties is that at present there is limited understanding of how the contact interface and the microstructures of contacting materials evolve during sliding. This evolution may include chemical reactions at the buried interface, grain growth and refinement, evolution of dislocation networks, interaction of dislocations with interfaces, chemical mixing etc. All these phenomena can contribute to energy dissipation (friction) and they can affect the dominant type and amount of wear. Changes taking place in the near-interfacial regions of the contacting materials are difficult to monitor experimentally in \textit{operando} because imagining techniques for buried interfaces under mechanical loads are still in their infancy. Computer simulations provide a powerful approach to investigating interfacial evolution and to discovering phenomena that control friction and wear. Here, I will discuss our developments of a multiscale simulation methodology to determine how materials evolve in sliding contacts.

In the first part of the talk I will focus on chemical evolution of frictional interfaces, a phenomenon referred to as chemical aging. Specifically, I will discuss the combined effects of chemical evolution of interfaces and of surface roughness on the origin of static friction, which is a highly debated topic in the field of tribology. Our approach combines density functional theory calculations of chemical reactions at interfaces, kinetic Monte Carlo simulations that extend simulation time scales to those that can be accessed in experiments, and boundary element method to extend simulation length scale and investigate multi-asperity contacts. For most solid/solid contacts, static friction increases logarithmically with time, a phenomenon known as aging. We discovered molecular mechanisms that are responsible for aging of silica/silica contacts in the presence of water and that are based purely on interfacial chemistry. By combing simulations with atomic force microscopy (AFM) experiments we identified the effects of contact pressure on both friction and aging, showing that aging is accelerated when the contact pressure is increased. Our model shows a quantitative agreement with AFM experiments on load-dependence of aging in single-asperity contacts. In addition, our model predicts that aging is a non-monotonic function of temperature and therefore the temperature can be used to control this phenomenon. Finally, we make predictions of how chemical aging will scale to large rough surfaces and how it will depend on the nature of the contact roughness.

In the second part of the talk I will discuss our developments of multiscale models of microstructural evolution of polycrystalline metals subject to mechanical loads. We combine molecular dynamics simulations with crystal plasticity and phase field models to determine microstructural evolution on experimentally relevant time scales. I will also discuss specific predictions from our models regarding the effects of grain size on chemical reaction mechanism of metal alloys. For instance, we have discovered an intermetallic alloy that can accommodate large plastic strain without help of dislocations due to formation of thin amorphous shear bands during deformation. This finding has important consequences for mechanical response because such intermetallics do not exhibit the classical Hall-Petch grain-size strengthening.

11:30 AM CP05.04.08
Icosahedral Quasicrystalline Nanoparticle Fabrication by Mechanical Approach
Samuel Showman,1,2 Anish Bhagwat,1 James Sanders,1 Kimmy Westover,1,2 Helen Hampkian2 and Chunfes Li3; 1Clarion University Department of Physics, Clarion, Pennsylvania, United States; 2Biology, Clarion University of Pennsylvania, Clarion, Pennsylvania, United States.

This paper reports our attempt to prepare icosahedral quasicrystalline nanoparticles (IQNP). It is well-known that, at the nanometer order, the properties of materials depend on their size. For example, the emission spectrum of quantum dots can be simply tuned by adjusting their size. Although nanoparticles of crystalline and amorphous structures have been reported, nanoparticles of icosahedral quasicrystalline structure, which combines a novel structure with nanometer size, have not.

It is believed that a mechanical approach is the easiest way to prepare IQNP. In our study, we proposed to grind alloy mechanically in to nanoparticles followed by size sorting using filtering. An alloy of Al\textsubscript{56}Cu\textsubscript{13}Fe\textsubscript{11} composition was used to experimentally establish this procedure. Alloy of this composition is closely related to the formation of pure icosahedral phase, although the alloy used in the present study is not of pure icosahedral phase. The alloy was ground for 40 hours and the existence of nanoparticles, particles smaller than 100 nanometers, was confirmed using Scanning Electron Microscopy (SEM). Such particles were suspended in methanol, forming a solution of 1 milligram per milliliter (1 mg/mL). This solution was then passed through a syringe filter. The passed solution was expected to contain particles with sizes smaller than the filter pore size and was subsequently passed through another filter with a smaller pore size. This filtering process began with filters of 5um pore size, and progressed through 1 um, and down to 0.45 um. The volume of the raw solution started with 1 mL and was maintained to this volume by adding extra methanol at different stages. SEM specimens were prepared by dispersing approximately 10 μL of the through-solution onto a silicon wafer and allowing to dry.

We were successful in filtering out nanoparticles, indicating that our procedure has been established, and is ready to be applied to an alloy of Al-Pd-Mn pure icosahedral quasicrystalline phase. During this process, we encountered the following problems and were able to establish effective solutions to overcome them.

We first began with hydrophobic polypropylene syringe filters. Upon examination of the specimen prepared with the flow through, it was frequently found that the desired particles were buried within unknown objects. The situation was worse with filters of a smaller pore size. The morphology of the objects resembled that of the filter fibers. This speculation was confirmed by Energy Dispersive X-ray Spectroscopy (EDS) analysis. The flow through of filter fibers is believed to be related to the presence of alloy particles in our solution, since repeated experiments with pure methanol did not cause this effect. With this knowledge, we switched to a stronger filter made of glass fiber. We found that the glass filter had little to no filter fiber flow through. The second problem we encountered is that the alloy particles obtained through filtering were mixed with salt (NaCl), which affected the examination of the nanoparticles by SEM. The effect became worse with filters of smaller pore size. We speculate that the salt is from the filter since salt was not observed on SEM specimens prepared from the raw solution prior to filtration. Several efforts were made to eliminate the salt. First, the filters were rinsed before use, although this turned out to also affect the integrity of the filters. Second, we scratched the silicon wafers with diamond paper and placed the particles on this relatively rough surface. Then we rinsed the sample with water with the aim of dissociating the salt, leaving the nanoparticles in the grooves. This was successful in removing almost all of the salt and allowing us to get a clear view of the desired particles.

11:45 AM CP05.04.09
Response of CuS Nanoparticle Additive in Ester Lubricant Under Electric Potentials
Ofir Friedman1, Chenxu Liu2, Yonggang Meng2, Yu Tian1 and Yuval Golan1; 1Ben-Gurion University of the Negev, Beer-Sheva, Israel; 2State Key Laboratory of Tribology, Tsinghua University, Beijing, China.

Nanomaterials have great potential as lubricating materials and for the development of advanced lubrication technologies. Moreover, applied electric field is considered to be of great interest and importance for controlling friction in systems with nanoparticle additives. Copper sulfide nanoparticles can be synthesized both as single nanoparticles and nanoplate arrays single by using single source, single surfactant technique and their surfactant coating can be re-organized in diferent structures by post synthesis thermal treatments.1 Surfactant coated CuS nanoparticle additives dispersed in diethyl succinate lubricant were studied in friction experiments under applied electric potential from -30 V to 30 V. A remarkable decrease in the coefficient of friction was observed upon application of an electric field perpendicular to the shearing interface. Friction tests indicate that the nanoparticles can reduce the friction coefficient of diethyl succinate lubricant by ~25%, from 0.24 to 0.18. When a negative potential lower than -14 V was applied, the friction coefficient markedly decreased to 0.05. Finally, different models were used for adsorption-settlement kinetics of nanoparticles implied that both the adsorption and settlement of CuS nanoparticles play an important role in the mass changes on the solid surface in the suspension of the nanoparticles. According to this research, shape controlled nanoscale lubricant additives are likely to have important technological importance in reducing and controlling friction in engineering systems.

The energy dissipated in a metallic frictional contact is largely converted into plastic deformation. The subsurface material is thereby exposed to extreme amounts of shear deformation and often forms layered subsurface microstructures with reduced grain size. We analyze the early stages of these processes with the aim of elucidating the elementary mechanisms for the formation of the subsurface microstructures by systematic model experiments and Discrete Dislocation Dynamics simulations. The simulations show how preexisting dislocations transform into dislocation structures within the stress field underneath a moving spherical contact. The crystallographic orientation is decisive for the formation of these structures and for dislocation transport with the moving contact[1]. Experimentally, we find a localized dislocation structure at a depth of ∼100-150 nm already after the first loading pass[2]. This dislocation structure is shown to be connected to the inhomogeneous stress field under the moving contact. Its generation and evolution under different conditions of load and loading rate are investigated. All subsequent microstructural transformations and the mechanical properties of the surface layer to some extent depend on this structure.


2:00 PM CP05.02 Microstructure Evolution and Deformation Mechanisms During High Rate and Cryogenic Sliding of Copper Xiang Chen1, Reinhard Schneider2, Peter Gumbsch1,3 and Christian Greiner1,4
1Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2Laboratory for Electron Microscopy, Karlsruhe Institute of Technology, Karlsruhe, Germany; 3Fraunhofer IWM, Freiburg, Germany; 4MikroTribologie Centrum μTC, Karlsruhe, Germany.

Frictional sliding induces a distinct discontinuity in the microstructure between a subsurface layer and the underlying bulk material, which strongly influences the tribological performance. Here, the strain rate and temperature dependence of such tribologically induced microstructure evolution was systematically investigated during reciprocating sliding of copper. It was found that an increase in strain rate and a decrease in temperature each result in a transition in the dominating deformation mechanism from dislocation slip to twinning-mediated plasticity at the very beginning of sliding. A sequence of deformation mechanisms was revealed under high rate and/or cryogenic sliding: First, nanoscale dislocation trace lines form beneath the surface during the first forward pass; Second, partial dislocation nucleation from the sliding surface accompanied by nano-twinning and abundant stacking faults in the backward pass; Third, formation of a nanocrystalline layer upon further sliding. Sliding induced surface roughening is found to assist partial dislocation nucleation from the surface during high rate and cryogenic sliding. Our results suggest that the sliding surface can act as an effective source of dislocations to initiate and accommodate associated plastic deformation, which may be explored to model the microstructure evolution during sliding.

2:15 PM CP05.03 Dislocation Mediated Plasticity in Sliding Friction From 10,000 to 2 nm Darcy Hughes 1 and Niels Hansen 2
1Consultant, Fremont, California, United States; 2DTU, Roskilde, Denmark.

Microstructural evolution induced by plastic deformation during dry sliding and frictional contact is quantitatively examined via electron microscopy over several length scales. Individual dislocations, medium to high angle and dislocation boundaries, crystal orientation/texture, as well as local changes in chemical composition were measured as a function of depth from the sliding surface. These quantified structures are analyzed within a universal framework developed for metals and alloys undergoing different modes of plastic deformation. New and prior statistical scaling laws are used to evaluate structural evolution and the gradient in microstructural size scale that develops with increasing depth from the surface. In the near surface regions crystallite sizes with an average of 5 nm and a minimum of 2nm are observed. This average size scale coarsens with increasing depth and is measured as a function of depth. A new scaling law connects the microstructural evolution of two measured structural parameters. In turn those structural parameters are related to strength parameters that estimate the flow stress utilizing a linear addition of the classical Taylor and Hall-Petch formulations. The gradient in flow stress with depth is used to evaluate the overlapping stress fields created by sliding deformation.

Mechanisms that promote this refinement and counteract structural coarsening are examined. Solutes and dislocations, in addition to the applied stress field and deformation temperature, are all important elements in structural refinement. Solutes may be present both in the original alloy or introduced via mechanical mixing during deformation. Their presence is important to suppress dynamic recrystallization. In the absence of dynamic recrystallization, coarsening occurs by the migration of sharp triple junctions between deformation-induced boundaries that enclose lamellar regions. Attached dislocations and solutes can suppress junction migration via pinning mechanisms. Solutes hinder migration via both their presence within high angle boundaries and within the matrix as they stabilize dislocations and low angle dislocation boundaries. The observed and continuous presence of dislocations is a key point. Dislocation mechanisms remain the dominant deformation mechanism even below 5 nm.


SESSION CP05.06: Materials Modification by Tribochemistry
Session Chairs: Clara Almeida and Izabela Szulflarska

Thursday Morning, April 25, 2019
PCC West, 100 Level, Room 102 B

8:00 AM CP05.06.01
Supercomputer Post-K Project “Challenge of Basic Science” in Japan and Its Recent Outcomes of Tribo-Wear Dynamics Induced by Chemical Reactions Momoji Kubo
Tohoku University, Sendai, Japan.

Supercomputer Post-K was constructed in 2011 in Kobe, Japan. Supercomputer K contains over 80,000 nodes and 700,000 cores and its calculation speed is 10^14 flops. Then, it won a championship in the supercomputer world ranking in June, 2011. However, in the supercomputer world ranking in June, 2018, supercomputer K ranks sixteenth. The ministry of education, culture, sports, science, and technology in Japan plans to construct new supercomputer post-K in 2021. The above ministry also started the “Post-K” projects for the development of Japanese-made simulation software on the supercomputer Post-K. Then, our proposed project “Challenge of Basic Science - Exploring Extremes through Multi-Physics and Multi-Scale Simulations” was adopted in June, 2016 and started in August, 2016. In this symposium, we introduce our supercomputer Post-K project and the recent outcomes of the tribology simulations by the supercomputer. The previous small-scale molecular dynamics simulations can clarify the super-low friction mechanism induced by the chemical reactions. However, the tribowear cannot be elucidated by the previous small-scale molecular dynamics simulations, because the tribo-wear simulations require huge amount of atoms. Super-large scale calculations by supercomputer and the molecular dynamics simulator optimized for supercomputer enable to simulate the tribowear dynamics induced by the chemical reactions. This is the paradigm-shift of the tribology simulation research. In the present presentation, we also discuss how the super-large scale simulations by the supercomputer “Post-K” will give the impacts on the tribology research.

8:30 AM CP05.06.02
Tribochemistry of Lubricating Materials by Ab Initio, QM/MM and High Throughput Approaches M. Clelia Righi
Department of Physics, Mathematics and Informatics, University of Modena and Reggio Emilia, Modena, Italy.
In Situ Modeling of Reaction Pathways and their Kinetics at a Sliding Solid-Solid Interface

G. Levita, and M. C. Righi, at graphene edges,
P. Restuccia, M. Ferrario and M. C. Righi

Ideal adhesive and shear strengths of solid interfaces: A high throughput ab initio approach In printing, Computational Materials Science.


Tribo-oxidation is an often observed but far from fully understood phenomenon during friction and wear, taking place by tribochemical reactions of the tribo-partners or the surrounding medium. These reactions in most cases lead to a change in the surface properties such as the chemical composition and the mechanical properties and consequently result in a different friction and wear behavior. The aim of our research is to elucidate the elementary mechanisms of tribo-chemically induced oxidation by paring polycrystalline high-purity copper plates with sapphire spheres. The experiments are performed at room temperature in a strictly controlled atmosphere with reciprocating linear sliding under mild tribological loading.

Our results show the formation of amorphous oxygen-rich cuprous-oxide (CuO) islands which are formed below the surface and grow to hemispherical amorphous/nanocrystalline cuprous-oxide clusters. We relate the growth of the clusters to the diffusion of oxygen on and in copper but the exact pathways of the oxygen are still elusive. After the islands have grown, they coalesce and form a continuous oxide layer on the surface, determining from then on the tribological properties of the contact. This oxidation process takes place at rates order of magnitudes faster than the native oxidation of copper in contact with the same environmental conditions. This works aims to understand the influence of the sliding velocity on the formation of these oxide clusters. We systematically vary the sliding speed from 0.1 to 5.0 mm/s and investigate the resulting microstructure. Scanning electron microscopy techniques are used in order to reveal the fundamental mechanisms of tribo-chemically induced oxidation. Once understood, this will help for tailoring the materials properties in order to achieve superior tribological performance.

This project acknowledges funding by the European Research Council (ERC) under Grant No. 771237. Furthermore, it was possible through funding by the German Research Foundation under Project GR 4174/1.

Microstructure Analysis of Fretting Damage in Nickel-Based Alloy 617 Ahmed Darwish1, Arman Ahmadi2, Farshid Sadeghi2, Korukonda L. Murty3 and Jacob Eappen1 1Department of Nuclear Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2School of Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States.

Nickel-based alloys exhibit superior thermo-mechanical properties and are currently being considered for structural components of very-high-temperature gas-cooled reactors (VHTRs). During the operation of a VHTR, the structural components are exposed to extreme conditions including high temperatures and stresses; they are also susceptible to corrosion from moisture and impurity gases such as carbon dioxide and methane. Fretting wear occurs in several VHTR components such as valve stems and seats, control rod drive mechanisms, and fuel handling mechanisms.

Recently, a set of in-situ fretting wear measurements have been carried out on a nickel-based superalloy – Inconel 617 [Ahmadi, A., F. Sadeghi and S. Shaffer (2018)] in helium and air environment at elevated temperatures. In this work, we perform microstructural analysis of the samples from these tests using confocal laser microscopy and scanning/transmission electron microscopy techniques. The surface roughness measurements show that small amount of oxides, which are more prominent at higher temperatures, inhibit wear damage. The elemental mapping using energy-dispersive x-ray spectroscopy (EDS) also reveal enhanced oxygen presence on the wear scars. We will finally describe the possible formation of complex carbides that have a deleterious effect on the long-time integrity of the structural components.

References
Extraordinary tribological properties of diamond and tetrahedral amorphous carbon (ta-C) make them promising candidates for protective coatings in a variety of industrial products such as bearings and seals. Their ultra- (0.01 < μ < 0.1) and super-lubricity (μ < 0.01) have been observed under boundary lubrication with water and oxygen-containing organic friction modifiers. State-of-the-art spectroscopic measurements provided evidence for chemical and structural modifications of ultrathin carbon layers that play a role in establishing near-frictionless states. However, the tribochemical mechanisms behind the formation of superlubrious tribolayers have not been fully understood yet. Here, we will present recent results of atomistic tribology simulations of diamond and ta-C surfaces in contact with various lubricant molecules.

Large-scale quantum molecular dynamics simulations reveal five different friction regimes for water-lubricated diamond (111) surfaces [1]. While water starvation gives rise to cold-welding and amorphization of the tribological interface, traces of water are sufficient to preserve crystallinity. This can result either in high friction due to cold-welding via ether groups or in ultralow friction due to aromatic surface passivation triggered by shear-induced Pandey reconstruction. As increasing amounts of water molecules, dense H/OH surface passivation also provides another ultralow friction state. For other low-index diamond surfaces [i.e. (110) and (100)], three additional friction regimes involving ether and keto oxygen were found [2]. The surface-orientation-dependent friction regimes are rationalized by the structural and energetic peculiarities of the different low-index surfaces. Experimentally observed superlubricity of ta-C under boundary lubrication with oleic acid and glycerol is explained by our atomistic model [1]. The presence of two reactive centers in the lubricants (e.g. carboxylic polar head and C=O double bond in oleic acid) allows them to concurrently chemisorb on both ta-C surfaces and bridge the tribogap. Sliding-induced mechanical strain triggers a cascade of molecular fragmentation reactions releasing passivating hydroxyl, keto, epoxy, hydrogen and olefinic groups. Similarly, glycerol’s three hydroxyl groups react simultaneously with both ta-C surfaces, causing the molecule’s complete mechno-chemical fragmentation and formation of aromatic passivation layers with superlow friction. Interestingly, our finding is not limited to oleic acid and glycerol, but applicable to other common friction modifiers.


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**SESSION CP05.07: Superlubricious Layers**

**Session Chairs: Koshi Adachi and Michael Moseler**

**Thursday Morning, April 25, 2019**

**PCC West, 100 Level, Room 102 B**

**10:30 AM *CP05.07.01***

**Atomistic Mechanisms of Superlubricity in Boundary-Lubricated Diamond and Diamond-Like Carbon Surfaces**

Takuya Kuwahara, Gianpietro Moras and Michael Moseler1, 2; 1Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany; 2Institute of Physics, University of Freiburg, Freiburg, Germany.

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**SESSION CP05.08: Triboelectricity and Late News**

**Session Chair: Mark Sidebottom**

**Thursday Morning, April 25, 2019**

**PCC West, 100 Level, Room 102 B**

**11:00 AM CP05.08.01**

**Is Triboelectricity Driven by the Flexoelectric Effect?**

Alex Lin, Christopher Mizzi and Laurence Marks; Northwestern University, Evanston, Illinois, United States.

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**11:15 AM CP05.08.02**

**Frictional Contact at the Nanoscale and Generation of Nanoscale Patterned Tribocharges**

Qiang Li1, Akshit Peer1, In-Ho Cho2, Rana Biswas1, 2 and Jaeyoun Kim1; 1ECpE & MRC, Iowa State University, Ames, Iowa, United States; 2DMSE, Ames Laboratory, Ames, Iowa, United States; 3CCEE, Iowa State University of Science and Technology, Ames, Iowa, United States.

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Actuation, length, stroke and actuation temperature. Novel approaches include using springs for radial compression, innovative biasing configurations and using the R-phase cycling to temperatures above and below the phase transformation temperatures under constant uniaxial strain conditions. Additionally, spatially resolved information was obtained in the case of the torsion specimens. The second aspect of this work will address the methodology adopted to design shape memory alloy springs along with results from comprehensive testing. The design considerations included multiple springs in limited operating volumes with requirements of forces exerted prior to actuation and following actuation, length, stroke and actuation temperature. Novel approaches include using springs for radial compression, innovative biasing configurations and using the R-phase transformation in NiTiFe springs. The discussion will also highlight appropriate modification of the theory in cases where substantial plastic deformation occurs during fabrication of the springs.

We have recently designed, fabricated and tested shape memory alloy elements in spring, tube and sheet forms for use in thermal switches, connect-disconnect mechanisms, deployable membrane telescopes and torsional tube actuators. The work has benefitted from in situ neutron diffraction at Los Alamos National Laboratory and Oak Ridge National Laboratory at stress and temperature in carefully selected experiments. The first aspect of this work will address implications for training (thermomechanical cycling for stable strain recovery in use) these alloys for cyclic aerospace applications and rely on experiments performed under (i) isothermal (both uniaxial and torsional deformation at constant temperature), (ii) isobaric (thermal cycling to temperatures above and below the phase transformation temperatures under constant uniaxial stress), and (iii) isostrain (thermal cycling to temperatures above and below the phase transformation temperatures under constant uniaxial strain) conditions. Additionally, spatially resolved information was obtained in the case of the torsion specimens. The second aspect of this work will address the methodology adopted to design shape memory alloy springs along with results from comprehensive testing. The design considerations included multiple springs in limited operating volumes with requirements of forces exerted prior to actuation and following actuation, length, stroke and actuation temperature. Novel approaches include using springs for radial compression, innovative biasing configurations and using the R-phase transformation in NiTiFe springs. The discussion will also highlight appropriate modification of the theory in cases where substantial plastic deformation occurs during fabrication of the springs.

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The hybrid nanomaterials formed by nanoporous metal and aqueous electrolyte have been considered competitive actuators since the concept appears in 2003. Motivated by this, here we study the impact of externally applied load on the actuation behaviors of nanoporous gold impregnated with an aqueous electrolyte. At no load, we observe the well-documented trend for a more positive electrode potential promoting elongation of the nanoporous body. For pure capacitive electrode processes on the clean surface, we confirm that the elastic response to external load is simply superimposed on the potential-induced elongation so that the strain per electric charge is invariant with the load. This is consistent with linear elastic behavior. Surprisingly, however, actuation in the regime of oxygen electrosorption responds strongly to loading: as the load is increased, the strain per charge first decreases and then inverts its sign. Furthermore, we demonstrate that the length change in response to lifting the oxygen adsorbate layer depends on the load that was present at the instant of oxygen-adsorption. We suggest that this “load memory effect” is a signature of the reorientation of local surface domains with anisotropic surface stress. We suggest that this “load memory effect” is a signature of the reorientation of local surface domains with anisotropic surface stress.

Li Alloy-Based Non-Volatile Actuators

Myoung-Sub Noh1,2, Seung-Hyub Baek1, Sangtae Kim1 and Chong Yun Kang1,2, 3

Center for Electronic Materials, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, Korea (the Republic of).

Actuators form the basis of the modern robotics industry, with applications ranging from microelectromechanical devices to medical or consumer electronics. Various actuator types including piezoelectric actuators, shape memory alloys and electrochemical actuators have been devised to meet the wide range of application needs. Especially, recent urge to develop humanoid robots and exoskeletons that mimic or aid human motions call for further development of a special kind of actuators called the artificial muscles. The requirements for successful artificial muscles include a large amount of strain (~10%) and large stress on the order of 100 MPa, preferably with low power consumption. Several novel actuator types have been suggested to serve as artificial muscles such as polymer-based actuators or electrochemical actuators. These actuators achieve successful integration into several robotics parts, with the characteristically large amount of strain, fast response time and below 3 V operation. Most artificial muscles developed so far, however, feature volatile actuation where voltage must be continuously supplied to maintain the actuated position; as soon as the input voltage is turned off, regardless of how big or small the operation voltage, the actuated position returns to its original position. Such volatile actuation is featured in most well-known actuators, including the piezoelectric, shape memory alloy-based, electrostrictive and ionic muscle actuators. For artificial muscles, this volatility indicates a significant loss of efficiency, as mimicking human motions involve a series of constant actuated positions. Such non-volatile actuation capability, however, has not yet been realized with many well-known artificial muscles. Here, we develop a non-volatile actuator with LiGe electrodes for artificial muscle. The novel actuator type consists of ion insertion electrodes so that the inserted ions pose stress on the electrodes that sustain even after power shut-off. The device consists of lithium germanide (LiGe) thin films deposited on both sides of a flexible polyimide (PI) substrate. The demonstrated device...
Bistable Electroactive Polymers and Compliant Electrodes

Bistable electroactive polymers (BSEPs) combine the properties of shape memory polymers and dielectric elastomer actuation at the rubbery state to generate rigid-to-rigid actuation. The variable stiffness could be obtained via glass transition or phase changing. The reversible melting-crystallization of polymer chains in the phase changing BSEP leads to a narrow temperature band to complete the stiffness change. A modulus change greater than 1000 fold can be achieved within a few degrees. Large actuation strains could be obtained. To drive the large-strain deformation, compliant electrode materials are also developed that maintain electrical conductivity at the large strains.

Heavy Lifting with Soft Materials—Layered Liquid Crystal Elastomer Actuators

Liquid crystalline elastomers (LCEs) are soft, anisotropic materials that exhibit large shape transformations when subjected to various stimuli. This shape morphing results when the net order of the material is reduced by external stimuli, such as heat, light, or electric fields. Here, we demonstrate a facile approach, lamination, to enhance the out-of-plane work capacity of these materials by an order of magnitude, to nearly 20 J/kg. Additionally, these materials can displace loads more than 2500x heavier than its own weight over 0.5 mm. The enhancement in force output is enabled by the development of a room temperature polymerizable composition used both to prepare individual films, organized via directed self-assembly to retain arrays of topological defect profiles, as well as act as an adhesive to combine the LCE layers. 1


Shape memory alloys such as NiTi intermetallic compounds exhibit a shape memory effect and a pseudoelastic effect owing to the transition between B2 austenite and B19(′) martensitic phases. Upon a large enough stress, dislocations will be formed and hinder the B2-B19(′)-B2 transformation that will diminish the shape memory effect. To improve the shape-memory and pseudoelastic performance, NiTi-based minor-doped, multicomponent and even in recent years high-entropy intermetallic compounds have been developed. However, because of the complex atom configuration and large lattice distortion in high-entropy materials, the structure, phase transition, mechanical response and deformation behavior of NiTi-based high-entropy intermetallic compounds need further investigations. Thus in this work, NiTi-based low-entropy (binary), medium-entropy (quaternary) and high-entropy (senary) intermetallic compounds were prepared by arc melting and casting (thereafter with homogenization), and their structures, mechanical properties and deformation behavior were then characterized. X-ray diffractions indicated that all the samples had a B2 austenite structure, but an expansion of unit volume was obviously noted in the high-entropy intermetallic compounds. Nanoindentation tests on different-orientation grains revealed the loss of anisotropy of mechanical properties in the high-entropy intermetallic compounds. The in situ SEM compression of low-entropy micropillars presented a pseudoelastic response and, upon yielding at a high load, typical long-distance slip deformation. However, the in situ SEM compression of high-entropy micropillars showed homogeneous barrel-like deformation without clear slip lines or plastic heterogeneity. The cross-sectional TEM observation revealed a short-distance activity of abundant partial dislocations rather than long-distance gliding of few complete dislocations in the deformed high-entropy micropillars.

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Mechanical Response and Deformation Behavior of NiTi-Based Low-, Medium- and High-Entropy Intermetallic Compounds

Heterogeneity. The cross-sectional TEM observation revealed a short-distance activity of abundant partial dislocations rather than long-distance gliding of few complete dislocations in the deformed high-entropy micropillars.

Phase inversion techniques, commonly used to fabricate filtration membranes, offer a mechanism to induce micro and nanoscale porosity in polymer materials, reducing their stiffness and impacting their mass elongation. Particulate additives can then be used to further modify the structure, and impart electrical properties. Together, macroscale properties of the composite can be tuned by controlling both the composition of the final material and its structure.

We demonstrate this using evaporation induced phase inversion of PVDF and explore the impact of non-solvent concentration and nano-scale ceramic particle loading on morphology. Particulate size and material are also varied, and show a dramatic impact on the structure of the pores present within the materials. This structure can be controlled from nano-scale voids to micro-scale foam-like openings. Testing shows how this morphology impacts the mechanical properties of these composites, determining how the materials can deform. Similar materials have already been used as battery separators. We look to further develop these porous composites to act as functional materials in soft electronics, using the filler to impart desired electrical properties such as conductivity, permittivity, and permeability, while maintaining low stiffness and high elongation.

Electroresponsive Homogeneous Polyelectrolyte Complex Hydrogels from Naturally Derived Polysaccharides

Homogeneous polyelectrolyte complex (PEC) hydrogels made from chitosan and carboxymethylcellulose were prepared in the LiOH/KOH/urea aqueous system through a freeze-thawing method. Following the treatments of sequential hydrolysis and physical crosslinking, the resulting hydrogels with superpower mechanical strength can operate as fast response actuators under electrical stimulus in salt aqueous solutions. The electromechanical behaviors of the hydrogels are strongly dependent on experimental parameters such as electric voltage, solvent constituents, pH, and ionic strength. It is proposed that the electromechanical deformation of hydrogel originates from a dynamic osmotic equilibrium effect taking place at the interface between the hydrogel and the surrounding medium, which is induced by the migration of ions throughout the gel network. In addition, programmable 3D shape transformations were obtained by using the PEC hydrogel with designed 2D geometric patterns. Moreover, the bending actuation behavior of the PEC hydrogel can propel an adjacent object to move forward. These hydrogels are expected to be used as underwater actuators for soft robotics and other smart biomimetic systems.
Stretching to the Future with Oxide Electronics

Madhu Bhaskaran, Sharath Sriram and Sumeet Walia; RMIT University, Melbourne, Victoria, Australia.

3:30 PM

van der Waals Oxide Heteroepitaxy for Transparent Flexible Electronics

Integration of Genetically Engineered Protein Fibers with Textile Scaffolds for Wearable Sensing Applications

The presentation will also discuss results from the various oxide based stretchable platforms for applications in sensing, optics, and memories. We have demonstrated a transfer process which is ubiquitous (can be used for any oxide coating), repeatable (and amenable to mass manufacture), scalable, capable of high integration densities (due to ability to micro/nano pattern) and which utilizes high performance oxide materials stretchable up to 15%. This process utilised the naturally weak adhesion of platinum to silicon, and this allows us to create electronics on a rigid substrate such as silicon and then peel off the layers to transfer onto a stretchable substrate. This process also results in a unique ‘micro-tectonic’ surface, creating opportunities to explore new stretchable device applications. This process has been successfully demonstrated using transparent indium tin oxide, zinc oxide, titanium dioxide, strontium titanate, and vanadium oxide.

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The presentation will also discuss results from the various oxide based stretchable platforms for applications in sensing, optics, and memories.

4:00 PM

van der Waals Oxide Heteroepitaxy for Transparent Flexible Electronics

Ying-Hao Chu1, 2; National Chiao Tung Univ, Hsinchu, Taiwan; 2Institute of Physics, Academia Sinica, Hsinchu, Taiwan.

Flexible electronics represents a fast-developing field and has a great potential to impact our daily life. In building up flexible electronics, the materials with controllable conduction, transparency, and good flexibility are required. van der Waals epitaxy (vdWE) involving two-dimensional layered materials can play a crucial role in the expansion of thin film epitaxy by overcoming the bottleneck of material combinations due to lattice/thermal matching conditions inherent to conventional epitaxy. Among the layered materials, mica is a well-known phyllosilicate mineral that can have a remarkable impact on flexible electronics. Due to the interplay of lattice, charge, orbital, and spin degrees of freedom, correlated electrons in oxides generate a rich spectrum of competing phases and physical properties. However, a generic approach to build up flexible electronics based on functional oxides is yet to be developed. In this study, we use a 2D material as the substrate. In this talk, we confine ourselves to the validity of vdWE of functional oxides on muscovite mica throughout this treatise. With such demonstrations, it is anticipated that MICAtronics, vdWE on mica, can reveal unusual properties and emergent phenomena in the realm of high-performance flexible device applications.

4:30 PM

Integration of Genetically Engineered Protein Fibers with Textile Scaffolds for Wearable Sensing Applications

Dalia Jane Saldanha, Bita Janfeshan, Zahra Abdali and Noemie-Manuelle Dorval Courchesne; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Smart materials and textiles with abilities to interact and respond to changes in their environment are becoming a need of the hour. Apart from being light-weight, flexible and portable, their fabrication into easy-to-read sensing devices can make the arena of diagnostics more accessible to the end-user. Among the options available today, engineered living materials, comprising a hybrid of living components that utilize energy sources to produce and/or secrete the bulk of the material and non-living components that confer novel properties, are gaining widespread popularity. One promising protein-based biomaterial we have studied in this project is the curli fiber system of E.coli. In this study, we report methods for effectively integrating curli nanofibers into commercially synthetic textiles to create functional wearable devices.

Curli fibers, in nature, constitute the non-pathogenic proteinaceous components of bacterial biofilms and can be genetically engineered to create a diverse range of stable and sensitive devices. These fibers form a high surface area porous network exhibiting unique self-assembly properties. They can be produced in various forms like gel, film, and powder while maintaining their properties. These systems have an edge over conventional organic polymers in that they are biocompatible and biodegradable while also being stable to enzymatic activities, detergent action and harsh chemical treatments. With properties that can be modulated through genetic, chemical and mechanical means, these materials find applications such as optical sensors in the diagnostic (e.g. wound infection) and personal care (e.g. blood glucose, stress hormone level) sectors.

A technique that showed great promise for integration of curli fibers into fabrics is vacuum filtration. In this work, we investigated the integration of protein curli fibers into various types of synthetic textile fabrics through the vacuum filtration technique. The filtration of curli-producing bacterial cultures onto the fabrics was followed by suitable washing and purification to separate the micro-organisms from the hybrid materials. With this method, we were able to load porous textile matrices with protein fibers throughout their cross-section, to create functional textile-protein composites. We optimized parameters affecting the extent of curli fiber incorporation onto the scaffold such as volume of the bacterial culture, porosity of the filtering fabric, and expression levels of the wild type or genetically engineered curli fibers. We also studied the microstructure and mechanical behavior of the fabrics before and after filtration. Microstructural analysis showed that the curli fibers were uniformly incorporated into the polymeric fibers of the fabrics over a large area. In some samples, self-assembly of curli fibers on textile fabrics was also observed. For further optimization, we studied the viscosity and rheological properties of the curli fiber gel obtained via vacuum filtration, and we explored suitable printing techniques such as screen or ink jet printing, as an alternative method for incorporating protein fibers into textiles. Last but not the least, curli fibers expressing a fluorescent sensing moiety were incorporated onto the textile scaffold, and we studied changes in functional activities before and after integration for potential development of this system into a fluorescent and wearable textile-based biosensor that is both accurate and user-friendly.

4:45 PM

Microstructured P(VDF-TrFE) Featuring Embedded Electrodes for Flexible Direction-Sensitive Strain Sensors

Philipp Schäffner1, 2; Jonas Grotten1, Maria Belegratis1, Andreas Tscheppe1, Martin Zirk1 and Barbara Stadlober1; 1Joanneum Research Forschungsgesellschaft mbH, Weiz, Austria; 2University of Graz, Graz, Austria.

Tomorrow’s Industry 4.0 environments raise a growing demand in self-sustained, flexible and low-cost sensors for versatile applications in process control as well as condition and energy monitoring. We present a new concept for direction-sensitive and flexible strain sensors based on the ferroelectric copolymer PVDF-TrFE and a single layer of interdigitated electrodes. Microstructured metal electrodes are formed on plastic substrates and embedded in the copolymer. Electric poling using the embedded electrodes (EE) allows the orientation of the ferroelectric domains primarily parallel to the P(VDF-TrFE)-substrate interface, thus having increased piezoelectric coupling with respect to lateral strains present in the surface plane. We employ a combination of (self-aligned) photolithography and electroforming to produce 2-10µm wide and up to 4µm high electrodes that are fully covered by screen-printed P(VDF-TrFE). Alternatively, we present a novel structuring method based on microfluidic channels hot embossed into P(VDF-TrFE) which are filled with conductive ink to form high aspect ratio EE.
Tensile tests with sensors having a footprint area of 1cm² were performed and compared with FEM simulations. The results show a highly linear charge response with respect to longitudinal strain, and the coupling strength depends significantly on the strain orientation in the surface plane. In conclusion, the use of the EE allows selectively resolving strain magnitude and orientation. Furthermore, bending at 90Hz excitation frequency yields an average power output of ~0.6µW per mm³ of active polymer volume, sufficient for stand-alone applications.

SESSION CP06.04: Poster Session: Smart Materials for Multifunctional Devices and Interfaces
Session Chairs: Shou-Yi Chang and T. Venkatesh
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

CP06.04.01 Thermoplastic Magnetorheological Elastomer for Fused Deposition Modeling—Filament Extrusion, Mechanical Properties and Magnetic Properties
Andrew H. Morgenstern, Thomas Calascione, Nathan Fischer, T.J Lee and Brittany Nelson-Cheesenman; Undergraduate School of Engineering, University of St. Thomas, Saint Paul, Minnesota, United States.

Magnetorheological elastomers (MREs) are unique smart materials of high elasticity and magnetic susceptibility. MREs are prominent for the high degree of mechanical deformation or changes in stiffness that can be induced by applying magnetic fields. While most MREs are made with thermoset elastomers, this research focuses on the development and testing of a thermoplastic magnetorheological elastomer (TMRE) for potential use as fused deposition modeling (FDM) filament. FDM, also known as 3D printing, is an additive manufacturing technique that consists of 1D viscous thermoplastic extrusions that create 2D layers that build up to a 3D part. This method of creating parts produces underlying anisotropies which can be tuned to control the properties of the final part. Printing could bring new functionalities and applications for TMREs due to new sub-structures that are available through FDM. Proposed applications include but are not limited to use in actuators, dampers, soft robotics, smart sensors and actuators, wearable technology and biomedical drug delivery. The first step in realizing such applications is the development of functional TMRE filament for FDM. Our TMRE was created utilizing solvent casting techniques to disperse isotropic magnetic particulate within a thermoplastic polyurethane matrix. A range of materials were explored to highlight the effects of particulate type and loading. Samples were created spanning two different magnetic particulate types (150µm iron & 2–4µm magnetite) and each with three different particulate loadings (20, 30, 40 wt%). The material was then extruded into FDM filaments with a Filameter. Filament width of the extruded filament samples was tracked and compared to evaluate the consistency of the extrusion process within the lab setting. Mechanical stress vs. strain curves of the extruded filaments were obtained using an MTS tensile tester. Magnetic hysteresis loops were acquired with a vibrating sample magnetometer (VSM). The analogous pure PU filaments were also extruded and tested as a control. Our testing indeed shows that altering the magnetic particulate type and its weight concentrations impacts both the magnetic and mechanical properties of the overall material. In general, the filament samples with magnetite particulate had higher diametric consistency and were stiffer than those with iron particulate. The heightened stiffness is likely due to the particulates smaller size and larger volume percentage of the magnetite given its lower density than iron. Additionally, samples with magnetite had higher magnetic susceptibility and coercivity but lower saturation magnetization than those with iron. Normalization of the saturation magnetization to compensate for the scaling of the particulate percentage indicates a consistent particulate dispersion and integration despite changes in its volume. Lastly, increasing particulate percentage increases both the mechanical stiffness and saturation magnetization of the samples, as expected. Future efforts will focus on further data analysis, magneto-mechanical testing, initial FDM printing tests, and cross-sectional imaging of the extruded samples to develop a robust explanation as to why the material functions in the way it does for insight and understanding when used in FDM. Despite being only the first step in understanding the functionality of this smart material, this step is critical for optimal utilization and realization in future applications.

CP06.04.02 All-in-One Piezoresistive-Sensing Patch Integrated with Micro-Supercapacitor
Yu Song and Haixia Zhang; Peking University, Beijing, China.

Portable and wearable sensors have attracted considerable attention, which could perceive and respond to ambient stimuli accurately. For the sake of solving the limited power supply and low integration, it is critical to develop and combine functional electronics with flexible energy devices. In this work, we designed an all-in-one sensing patch integrated with piezoresistance sensor and micro-supercapacitor with the porous CNT-PDMS elastomer. Taking the advantage of porous structure with piezoresistivity and elastomer with electrochemical performance, the piezoresistance sensor shows high sensitivity (0.51 kPa⁻¹) and wide detection range as functional fraction, and micro-supercapacitor maintains excellent areal capacitance and cycling stability after 6000 cycles as energy storage fraction, respectively. Assembled with piezoresistance sensor and micro-supercapacitor, the sensing patch could be easily attached on the epidermal skin for joint and muscle monitor with the corresponding resistance response. With high sensitivity and mechanical robustness, such sensing patch could be further utilized as a 3D touch in user identification and safety communication through feature parameter extraction and signal decoding. After packaged into the sensing patch matrix, it could be achieved for static pressure sensing and dynamic tactile trajectory. Therefore, the all-in-one sensing patch shows feasibility in real-time pressure recognition and human-machine interfaces.

CP06.04.03 Preparation of Fabrics with Smart Directional Water-Transport Property
Lihong Lao, Dahua Shou, Yuen Shing Wu and Jintu Fan; Cornell University, Ithaca, New York, United States.

Clothing provides a microclimate between the body and the external environment, and acts as a barrier for heat and vapor transfer in between. In sweating conditions, in order to maintain the thermal comfort, fabric next to the skin should not only absorb liquid rapidly but also transport it through the fabric promptly to avoid the discomfort of the fabric sticking to the skin. On the other hand, in the raining weather, the fabric next to the environment is desired to prevent the water passing from the environment to the skin, and thus should possess water-resistant or water-proof properties. Therefore, there’s a demand to design a smart fabric material that has an asymmetric wettability and could directionally transport water from the skin to the environment, but minimize the transport in the reverse direction.

In this project, we worked towards this goal — endowing asymmetric wettability on breathable fabrics to enable directional (differential) water transport properties. We used a combination of superhydrophobic finishing and plasma selective treatment to create gradient wettability channels through the fabric thickness. While these channels were served for directional liquid transport, the untreated larger surface remained superhydrophobic, therefore could still provide thermal comfort and water-resistant properties next to the skin and environment, respectively. The directional water transport ability was confirmed by a home-made measurement device. Additionally, SEM, TGA, chemical analysis, and contact angle measurements were performed to determine the surface structure and wettability of the fabric after various modification conditions.

CP06.04.04 Hydrothermal Synthesis and Characterization of Cesium Lead Halide (cspbX3) Perovskites for Optoelectronic Applications
Sahaya D. Babu and Xavier Sahaya Shajan; 1Department of Physics, Chettinad College of Engineering and Technology, Karur, India; 2Department of Physics, PSN College of Engineering And Technology, Trurnveli, India.

The outstanding optoelectronic properties of inexpensive and solution-processable hybrid metal halide perovskites have brought them to the forefront in many research fields, such as solar cells, light-emitting diodes, photo detectors, and lasers. One of the main advantages of these materials is that its optical band gap can be easily tuned by altering the constituent elements. The success of these materials quickly led to the synthesis of organic/inorganic hybrid perovskites, and later also as purely inorganic cesium-based perovskites. Nanocrystals exhibit high photoluminescence quantum yields (PLQY’s) and offer an inherent way to tune the optical properties through size- and dimensionality-dependent quantum confinement. Currently, a limited number of synthetic methods are available for the preparation of CsPbX₃ NCs. In this regard, we have been made an attempt to synthesize cesium lead halide perovskites through simple hydrothermal method. The prepared nanomaterials were characterized by various analytical techniques. XRD and Raman analysis shows perfect crystalline nature of cesium perovskite and its morphology was obtained from FESEM and TEM analysis. Band structure properties of cesium halides were attained from XPS and UPS analysis. Details will be presented.
Dynamic Surface Topography in Micro-Objects and Films

Mustafa K. Abdelrahman, Hyun Kim, Patrick Ondruske, Jimin Maeng and Taylor Ware; The University of Texas at Dallas, Richardson, Texas, United States.

Strategies to induce dynamic surface topography may enable new engineering devices where friction, fluid flow, or cell attachment is a property that needs to be controlled on-demand. There are multiple ways to create polymeric materials where the surface topography can be induced to change in response to a stimulus. For example, shape memory polymers can switch from smooth to rough on heating, but require mechanical programming, limiting this effect to only objects that can be easily deformed such as films. Also,
liquid crystalline networks could induce surface topography changes without a programming step; however, they require a constant energy source in order to keep the surface topography from returning to its original state. They also require an initial alignment step, which further confines this ability. Here we describe a versatile strategy to significantly and permanently alter the surface topography of films, microstructures and microphones without any mechanical programming step or initial alignment. Specifically, we use a radical thiol-ene reaction to build semi-crystalline polymer networks from low molecular weight monomers. Crystallization of the network occurs concurrently with polymerization and produces a material with built-in stresses. On heating through the melting point of the network, these initially smooth materials, having an average roughness of 10 mm, form peaks and valleys, reaching an average roughness of 500 nm. We have been able to produce this effect in films, micro-molded structures, and microphones. The magnitude of the roughness can be controlled by altering either the melting point of the network, the crosslink density, and/or the polymerization temperature. For example, we show that the closer the polymerization temperature is to the substrate's melting temperature, the less rough the substrate becomes after being heated to its melting temperature. This allows us to pattern roughness by simply polymerizing different portions of the substrate under various temperatures. This control will allow us to tackle major engineering challenges in the areas of micro fluids, self-cleaning films, bio-adhesion and cell growth.

CP06.04.10
Effect of Zn Substitution on Structural, Dielectric and Magnetic Properties of Cobalt Ferrites and Their Applications

Tammam Mariani1, Kazu Haniu2, Nazru Islam Khan3, and Shamima Choudhury1
1: Department of Physics and Astronomy, University of Toledo, Toledo, Ohio, United States; 2: Department of Physics, University of Dhaka, Dhaka, Bangladesh; 3: Material Science Division, Bangladesh Atomic Energy Center, Dhaka, Bangladesh.

A series of Co1-xZnxFe2O4 ferrite with (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5) compositions were synthesized using the standard double sintering ceramic technique, sintered at 1050°C for 2 hours. Substituting Zn in place of Co influenced the structural, dielectric and magnetic properties of CoFe2O4 samples. Structural analyses were carried out using X-ray diffraction (XRD). The X-ray diffraction pattern confirmed the single-phase cubic spinel structure and the sharp peak revealed that the samples are in good crystalline form. The lattice parameters were calculated for each composition and found to increase with Zn substitution. A significant increase in density and subsequent decrease in porosity was observed with increasing Zn content. The grain size of the samples was reduced by enhancing the Zn concentration. The dielectric constant (ε') of the sample is found to decrease with increase in frequency exhibiting normal dielectric behavior. Dielectric relaxation peaks were observed for the frequency dependence of dielectric loss tangent curves. The observed dielectric properties were explained on the basis of electron conduction mechanism. The variation of the resistivity versus temperature was also studied and the dielectric constant of the system has a variation quite similar to that of the resistivity. VSM measurement confirmed that the magnetizations of all the samples were saturated. Saturation magnetization and coercivity were estimated with variation of Zn content. These effects are due to facilitation of demagnetization by substitution of the non-magnetic Zn ions. Permeability was found to decrease with increasing in Zn content. The characteristics of electromagnetic, excellent chemical stability, mechanical hardness, low coercivity, moderate saturation magnetization and high anisotropy constant suggested Cobalt Ferrite a good candidate for synthesizing and investigation to contribute as dielectric, magnetic, multifunctional material and in storage devices for the advancement of science and technology.

CP06.04.11
Outstanding Performance of CuCo2O4 as an Electro catalyst for Urea Oxidation

Camilla Zequine1, Fangzhou Wang2, Xianglin Li3, Khamis Siam4, Pawan Kabol5 and Ramkumar Gupta2
1: Pittsburgh State University, Pittsburg, Kansas, United States; 2: Department of Mechanical Engineering, University of Kansas, Lawrence, Kansas, United States.

Urea oxidation reaction (UOR) brings a possible solution to solve the energy crisis in the world. Fuel cells have been used UOR to generate hydrogen with lower potential compared with water splitting, decreasing the costs of energy production. Urea is abundantly present in waste agricultural, and in industrial and human wastewater. Providing a generation of Hydrogen, this reaction provides a pathway to eliminate urea as a hazard in the environment and people's health. Herein, nanostructure 3D flower like CuCo2O4 grown on Ni foam were synthesized as an electrocatalyst for urea oxidation to generate hydrogen as a green fuel. The synthesized electrocatalyst was characterized using X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. The electroactivity of this material toward the urea oxidation in alkaline solution was evaluated using electrochemical measurements. The results for UOR confirm the applicability of the electrode as promising electroactive material for hydrogen production. Nanostructured CuCo2O4 grown on Ni foam requires a potential of 1.36 V in 1 M KOH with 0.33 M urea to deliver a current density of 10 mA/cm2. The electrode is electrochemical stable for over 15 hours of continuous measurements. The high catalytic activities for hydrogen evolution reaction make CuCo2O4 electrode as a bifunctional catalyst. The two electrode electrolyzer demands a potential of 1.52 V which is 190 mV less than that for the urea-free counterpart. Our study suggests that CuCo2O4 electrode can be a promising pathway to efficient UOR catalysts used in fuel cells with low-cost hydrogen generation.

CP06.04.12
Polyampholyte Micgels as Ionic Traps for Proteins

Wenjing Xu1,2, Andrej Rudov1,4, Ricardo Schroeder2,1, Igor Potemkin3,1, Walter Richtering4,1 and Andrij Pich3,4
1: DWI-Leibniz Institute for Interactive Materials, Aachen, Germany; 2: Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany; 3: Physics Department, Lomonosov Moscow State University, Moscow, Russian Federation; 4: Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany.

Polyampholyte microgels contain both acidic and basic functional groups and are able to change their charge as function of the pH. Their particle sizes under aqueous state swell at pH 4 due to electrostatic repulsion and collapse at pH 11 due to electrostatic attraction. Their swelling and shrinking can be controlled by changing the pH. Therefore we aimed to synthesize polyampholyte microgels as carriers to achieve a triggered uptake and release of guest molecules. Microgels as carrier systems to transport guest molecules have attracted great attention in the past years. Their ability to bind and release guest molecules upon changing the outer stimuli is making them interesting for a wide range of applications especially in biomedical fields. It is well established that microgels interact with guest molecules via different pathways as covalent binding, hydrophobic interactions and electrostatic forces. In case of the interaction between polyelectrolytes, electrostatic forces are of greater importance. Therefore we are trying to synthesize polyampholyte microgels as carriers to achieve a triggered uptake and release of guest molecules. Polyampholyte microgels contain both acidic and basic functional groups and are able to change their charge as function of the pH. Their particle sizes under aqueous state swell at pH 4 due to electrostatic repulsion and collapse at pH 11 due to electrostatic attraction. The existence of an isoelectric point is another important characteristic feature of polyampholyte microgels revealing at which pH the charges are equal and the overall net charge become zero. In this research we synthesized new microgels with defined charge localization and various architectures (random, core-shell and Janus-like microgels) with free radical precipitation polymerization. Together with the help of computer simulations, we investigated the swelling and collapse of the microgels with possible shape variation as function of different external stimuli. In addition we studied the interaction of the synthesized microgels with the model protein cytochrome c at different pH values and different internal structures.

Development of Thermal Insulation Materials for Buildings with X-Ray and γ-Ray Shielding Function

Teruyoshi O. Hirano1, Yuki Katakanai1, Satoro Hashimoto1, Ichiro Hatusumari1, Tsukaru Nishisunou1, Naoki Yamashita1, Takumi Iwasaka2, Yako Yamashita1 and Yasuyuki Mori2; 1: GGG Inc, Tokyo, Japan; 2: MAKUZO Co., Ltd., Fukushima, Japan.

In the accident at Fukushima Daiichi Nuclear Power Station, many radioactive materials were released into the environment field. In the future, materials with radiation shielding property will be required for a long period. We have developed and reported Anti-Sievert® Concrete with enhanced shielding function as construction material1. Anti-Sievert® Concrete has a shielding function of about 3 times as compared with ordinary concrete for X-ray (200 kV) and shows strength exceeding 40 N / mm2. For building materials other than concrete, the application of advanced shielding function is required. In this report, we improved the function of shielding effects of radioactive materials and radiation on Rock-Wool, which is a typical heat insulating material widely used for many buildings. This material is a blend of Anti-Sievert® (high density ceramics material) with shielding function with other materials with shielding function. For improving the shielding function, it is required to increase the content of Anti-Sievert®. However, in order to realize the heat insulating function, it is essential to be porous. We developed heat insulating materials with practical shielding function by properly balancing these conflicting design values. In the present formulation, it has a shielding function of about 0.2 to 0.3 mm (100 kV) equivalent to lead in Anti-Sievert® Rock-Wool with a thickness of 50 mm. This characteristic corresponds to the shielding functions used for medical X-ray transmission photography equipment. Continue to improve the shielding function and report materials with shielding function of practical level that can be widely used for buildings. We think that this material is extremely useful in the Fukushima area.

Shape memory materials traditionally utilize temperature or environmentally dependent phase transitions in order to return from a deformed state. Alternatively, magnetic shape memory alloys have long been investigated, as they can be deformed by magnetic fields rather than environmental conditions; however, these alloys suffer from the drawback that they exhibit very small strains. This has led to recent developments in magnetoreheological elastomers (MREs), which can exhibit significantly greater strains. Our research focuses on the processing of a thermoplastic MRE by solvent casting a polyelectrolyte (PE) elastomer with magnetic particulate for fused deposition modeling (FDM) applications. FDM, commonly referred to as 3D printing, is a valuable manufacturing technique that allows for the creation of parts with inherent anisotropies. For the case of an MRE, FDM allows for the production of structures with tunable magnetic susceptibility along different axes. In these composites, the degree of particulate dispersion significantly affects the isoropy of material properties, which becomes increasingly important when small material volumes are used, such as in FDM. Incorporating solvent casting as a versatile method of producing polymer composites will allow for greater control over the particulate addition method, leading to a higher degree of dispersion when compared to a polymer melt. For our purposes, composite thin films were produced in order to examine effect of wet vs. dry addition of particulate on dispersion, while thicker samples were produced to study the porous structures obtainable by utilizing different drying methods. The solvent used in producing the PU composites was dimethylformamide (DMF). Preparation of polymer solutions included dissolution of PU in DMF to 20 w/v% followed by addition of the magnetic particulate. The particulates used were <150 µm iron powder and 2-4 µm magnetite powder. Composites solutions were made to concentrations of 20, 30, and 40 w/w% particulate to polymer by addition of either dry particulate or particulate pre-suspended in DMF. Drying conditions included room temperature air drying, or a dehydrator, or drying in a vacuum oven. Wet addition of magnetic particulate led to smaller clump sizes and improved dispersion, while dry addition led to larger clump sizes and poorer dispersion. All drying techniques prominently affected the degree of porosity in the resulting composite. Future inquiry will focus on the effects that the porosity of the composite, as a result of drying technique, has on further processing and manufacturing; ensuring that the effect of addition method on the dispersion of particulate in thicker samples is equivalent to that found in thin films; and understanding the impact that each of these factors will have on components manufactured by FDM.

**CP06.04.15**

**3D Numerical Simulation on the Effect of Surface Morphology for Highly Sensitive Ion-Sensitive Semiconductor Nanowire Sensors**

Yunsung Cho, Jeong-Su Kim, Geon-Gu Ji, Jin-Tea Kim and Yeon-Ho Im; Chonbuk National University, Jeonju-si, Korea (the Republic of).

Semiconductor nanowire ion-sensitive field effect transistor (NW-ISFET) has attracted considerable attention as a next-generation sensor platform for a wide range of chemical and biological applications. Despite their potential applications, highly reliable sensing performance of NW-ISFET is regarded as one of the main bottlenecks for commercialization of this technology. This issue may be mostly due to a lack of understanding of sensing mechanisms. To address this issue, we have performed 3D device modeling to capture the detailed aspects of NW-ISFET sensing mechanisms with the change of nanowire surface morphologies in chemical and biological applications. At the electrolyte interface between nanowire and liquid, a specific site binding model and Gouy-Chapman-Stern theories were applied in order to consider the realistic ion-screening effects via the electrical double layer. Meanwhile, 3D electronic transports on the nanowires with different surface morphologies were coupled with the electrochemical models. Finally, the simulation results are verified through comparison of our previous experimental data. It was concluded that the main aspects of NW-ISFET sensing performances were captured with our 3D numerical simulation according to the change of nanowire surface morphology. Finally, the detailed origins of the NW-ISFET sensing mechanism will be discussed. We believe that this work can give better insights to improve the reliability of chemical and biological NW-ISFET sensors.

**CP06.04.16**

**3D Printing of Carbon Nanotube-Based Electrically Conductive Nanocomposites**

Rasool Bayvanjhangang, Michael Hilli and Parisa Pour Shahid Saeed Abadi; Michigan Technological University, Houghton, Michigan, United States.

3D printing is a novel fabrication technique for constructing structures with complex geometries and material characteristics. 3D printing of conductive structures could potentially create material systems with unique combination of properties including electrical conductivity, mechanical integrity, and electrochemical properties. Such unique properties render the structures excellent for applications such as micro-electronics, robotics, sensors, and actuators, etc. Carbon nanotubes (CNTs) are excellent candidates for filler in inks to be used in 3D printing of conductive structures. The high aspect ratio of 1D CNTs makes them superior to zero-D materials such as metal nanoparticles and 2D materials such as graphene in applications such as fibrous constructs or linear actuators. Here we report 3D printing of carbon nanotube-based inks into geometries not possible with methods other than 3D printing. Our fabrication process consists of preparing a printable mixture of a polymer such as polydimethylsiloxane (PDMS) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT) and CNTs by ultrasonication, and then printing in a medium such as gelatin. We report unique properties ranging from mechanical to electrochemical including stiffness, elasticity, and capacitance.

**CP06.04.17**

**Memristive Nanowire Neural Network for Neuromorphic Computing**

Nikita N. Gaur, Jack D. KendallIII, Suhas Kumar3 and Juan C. Nino3; ‘Rain Neuromorphics, Redwood City, California, United States; 2Hewlett-Packard Company, Palo Alto, California, United States; 3Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, United States.

The traditional Von Neumann computing architecture is reaching fundamental limits in terms of energy efficiency and scalability, especially with increasing data-intensive applications. Hence, it is imperative to look for alternative computing paradigms with coellected computation and memory. One promising example is neuromorphic hardware. These architectures are inspired by the massively interconnected architecture of biological brains, and have so far demonstrated improvements in scalability, robustness, and computational efficiency over traditional architectures. Resistive memories such as memristors (RRAM) and PCRAM are well suited for the artificial synapses of neuromorphic architectures, since they are non-volatile and can store multiple resistance states, similar to biological synapses.

In this work, a novel neuromorphic architecture called the Memristive Nanowire Neural Network (MN3) is proposed.2,3 The MN3 consists of an array of neural nodes interconnected using a randomized network of memristive nanowires. Each nanowire comprises a conductive core, which transmits signals between neurons, and a memristive shell, which forms memristive synapses with the neural nodes in the array. The techniques for fabricating such an architecture have been demonstrated along with static and dynamical switching characteristics. Hafnium oxide (HfO2)-based RRAM memristors have been studied for this work. Detailed analysis using complementary techniques such as EDX, XPS, FE-SEM, and HR-TEM will be further presented to 1) understand how structural and microstructural properties are affected by the electrical characterization of such films and 2) identify important parameters to further improve the devices. Simulation results showing improvements in the scalability of the MN3 architecture over traditional crossbar architectures will also be presented.


**CP06.04.18**

**Defected-Activated Cobalt-Iron-Layered Double Hydroxide (Co-Fe LDHs) as Highly Efficient Electrocatalyst for Enhanced Oxygen Evolution Reaction**

Cui Ye; Zhejiang University of Technology, HangZhou, China.

Since the oxygen evolution catalysis process is vital yet arduous in the energy conversion and storage devices, engineering the earth-abundant nanomaterials with superior electro-catalytic activity remains desired and tough for effective oxygen evolution reaction (OER). Herein, we reports a prism-like cobalt-iron-layered double hydroxide (Co-Fe LDHs) utilizing a facile cation-exchange strategy accompanied with hierarchical nanoflake shell and well-defined interior cavity. Instead of the conventional LDHs commonly referred to as 3D printing, is a valuable manufacturing technique that allows for the creation of parts with inherent anisotropies. For the case of an MRE, FDM allows for the production of structures with tunable magnetic susceptibility along different axes. In these composites, the degree of particulate dispersion significantly affects the isoropy of material properties, which becomes increasingly important when small material volumes are used, such as in FDM. Incorporating solvent casting as a versatile method of producing polymer composites will allow for greater control over the particulate addition method, leading to a higher degree of dispersion when compared to a polymer melt. For our purposes, composite thin films were produced in order to examine effect of wet vs. dry addition of particulate on dispersion, while thicker samples were produced to study the porous structures obtainable by utilizing different drying methods. The solvent used in producing the PU composites was dimethylformamide (DMF). Preparation of polymer solutions included dissolution of PU in DMF to 20 w/v% followed by addition of the magnetic particulate. The particulates used were <150 µm iron powder and 2-4 µm magnetite powder. Composites solutions were made to concentrations of 20, 30, and 40 w/w% particulate to polymer by addition of either dry particulate or particulate pre-suspended in DMF. Drying conditions included room temperature air drying, or a dehydrator, or drying in a vacuum oven. Wet addition of magnetic particulate led to smaller clump sizes and improved dispersion, while dry addition led to larger clump sizes and poorer dispersion. All drying techniques prominently affected the degree of porosity in the resulting composite. Future inquiry will focus on the effects that the porosity of the composite, as a result of drying technique, has on further processing and manufacturing; ensuring that the effect of addition method on the dispersion of particulate in thicker samples is equivalent to that found in thin films; and understanding the impact that each of these factors will have on components manufactured by FDM.
both experimental and theoretical efforts are being directed to understand the gas-sensing properties of hydrogen (H2) gas on ZnO films. The theoretical study is based on a combination of density-functional theory (DFT) with non-equilibrium Green’s function (NEGF) formalism. A focus was given to assess the catalytic effects of noble metals versus other low-electronegativity transition metals (e.g., Au, Pt, Ag, Pd, and Fe) were put, separately, as ad-atoms on ZnO nano-ribbons (ZnO-NR) on the transport properties and thus gas-sensing. While the results are in favor of chemisorption to take place in all the instances of the studied catalysts, Pt and Pd in particular have shown more coordination with the ZnO bed (stronger binding energies). Consequently, they both enormously affect the density of states at Fermi level and yield the largest deviations in IV-curve, from before to after the landing of H2 molecule. In case of Pt catalyst, the sensor’s response is found to be the largest in detecting H2 gas molecule. Tests of chemisorption using Pt catalyst to other gases (e.g., O2, N2, CO2; and H2S) have confirmed its great selectivity toward the detection of H2 gas. The experimental findings are in excellent agreement with the theoretical predictions.

**CP06.04.20**

**Printing Direction Influence in Properties of Additively Manufactured Functional Ceramics**  
Luis Chavez1,2, Bethany R. Wilburn1,2, Luis C. Delfín1,2 and Yirong Lin1,2  
1 Department of Mechanical Engineering, The University of Texas at El Paso, El Paso, Texas, United States; 2 W. M. Keck Center for 3D Innovation, The University of Texas at El Paso, El Paso, Texas, United States.

An increasing trend in the use of “green” energy sources for electricity generation has been observed in recent years. Despite this, electricity generation continues to be highly dependent on fossil fuel energy sources all around the world. As a result, the efficiency of energy conversion systems is critical for low emissions. Meticulous monitoring of the operating conditions of these systems can aid in achieving higher efficiencies. Piezoelectric materials are great candidates for this type of application due to their pressure and temperature sensing capabilities as well as their ability to withstand harsh environments. Barium titanate, BaTiO3, is one of the most prominent piezoelectric ceramics. One of the main drawbacks of implementing piezoelectric ceramics in these systems is their geometry and size constraints. Current manufacturing methods of these ceramics do not allow for custom complex designs. A novel solution to this issue has been the implementation of additive manufacturing to fabricate piezoelectric ceramics with complex geometries. However, most of the recent efforts have yielded low density parts and therefore weak mechanical and electrical properties. The purpose of this research project was to fabricate BaTiO3 using an ExOne M-Lab binder jetting 3D printer to study its dielectric and piezoelectric properties as a function of the printing direction. The morphology of the samples as well as the dielectric and piezoelectric properties were characterized in the normal and parallel orientations to the printing direction. Samples achieved a density of 36.8% after sintering. Meanwhile, samples that were electroded in the parallel direction to the printing layers presented an average dielectric constant of 34.6% and a piezoelectric constant of 70.5% of the theoretical properties of BaTiO3. Additionally, improvements in dielectric and piezoelectric constants of 20% and 13.5%, respectively, were observed for the samples tested in the normal direction to the printing layers. These results show that despite low densities, ceramics with high piezoelectric coupling coefficients can be fabricated through binder jetting additive manufacturing. Further optimization in printing parameters and powder used for the fabrication must be performed to achieve higher densities in the final parts.

**CP06.04.21**

**A Solid-State Light Emitting Device with a Coplanar Structure**  
Yue Kuo; Texas A&M Univ, College Station, Texas, United States.

The solid state light emitting device (SSI-LED) was reported by the author's group recently (1). Upon the application of a gate voltage, the broad band warm white light is emitted from a large number of nano-sized conductive paths formed from the dielectric breakdown of a MOS capacitor on a p-type Si wafer. The light emission principle is the thermal excitation of the conductive path upon the passage of a current (2). In spite of the difference in gate dielectric materials and process conditions (3), all lights are emitted over the same visible to near IR wavelength range. The SSI-LED also shows unique electric characteristics similar to those of an antifuse or a diode (4). However, since all SSI-LEDs on the same substrate share the common ground electrode, the crosstalk is unavoidable, which is a potential problem in practical applications.

In this paper, a new coplanar structured SSI-LED is reported. Each device has its own gate and ground electrodes both of which are located on the same side of the substrate. Since devices can be isolated with LOCOS, trench, or other methods, there is no issue of crosstalks among different devices. The emission spectrum of the new device is the same as that of the device with gate and electrodes located on different sides of the substrate. The former has a higher intensity of the emitted light than the latter has due to the formation of more conductive paths. The structure of the new device and the pattern of the current flow will be used to explain the improvement of the light emission. Potential applications of the new device will also be examined.

Shumao Zhang is acknowledged for preparation and characterization of SSI-LEDs in this paper.


**CP06.04.22**

**Fabrication of Vanadium Dioxide Thin Films for Device Applications**  
Arun M. Umarij, Devanshi Bhardwaj and Inyalot J. Tadeo; Indian Institute of Science, Bengaluru, India.

VO2 being a transition metal oxide is the most fascinating material of research as it shows a semiconductor to metal transition (SMT) near to room temperature (T~68 °C). It undergoes a structural change from M1, monoclinic phase (Space group: P21/c) to R, tetragonal phase (Space group: P4/mmm). Due to this phase transition, it is used for various applications like smart windows, metamaterial, bolometers, etc. In here, we report the synthesis of device quality VO2 thin films. Various methods like home-built Ultrasonic Nebulised Spray Pyrolysis of Aqueous Combustion Mixture (UNSPACM), Chemical Vapor Deposition (CVD), Pulsed Laser Deposition (PLD) and DC Reactive sputtering have been employed for the synthesis of phase pure VO2 thin films. The structural characterization has been carried out by XRD and Raman measurements which confirms the M1 phase of VO2 at room temperature followed by high-temperature measurements to study the phase change. Temperature-dependent resistance measurements confirm the SMT transition at T~68 °C with a three-four order of magnitude change in resistance. Temperature-dependent IR measurements show ~80% change in reflectance across the phase transition where the thin film acts as an IR reflector (T~67°C). Effect of dopant (W, Mo, Sc, Ce etc.) has been studied where the T~SM was reduced to 25 °C with 2 at % W doping. Our preliminary attempts to make metamaterials will also be presented.


**CP06.04.23**

**Metal-Organic Framework Cu-BTC (HKUST-1) in Poly(L-lactide) for Synergetic Effects of Nucleating Agents, Reinforcement and Toughening Resulting in Surprising Shape Memory Effects**  
Hamideh Rezvani Alanagh1,2, Babak Akbari1 and Dinamjan Pun1; 1 Department of Life Science Engineering, Faculty of New Sciences and Technologies, University of Tehran, Tehran, Iran (the Islamic Republic of); 2 Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Composite films exhibiting remarkable shape memory effects are prepared via solution casting of Metal-Organic Framework, Cu-BTC (HKUST-1) in poly(L-lactide) (PLLA)
Optically Switchable Photoelectron Injection from Perovskite Nanorods for Wavelength-Distinguishable UV Photodetector

To the best of our knowledge, this work is the first one to explore the MOF induced shape memory effect in polymers. It is found that HKUST-1 is acting as a nucleating agent to trigger the crystallization of PLLA for ensuring the entropy needed for the shape memory behavior; this results in recovery ratio, and fixity ratio to be about 100 %, and 95%, respectively with 5% Mwt filler in elongation of 25%. Aspirin encapsulated in HKUST-1 reinforced PLLA is investigated to clarify the mechanism, and concluded that the supposed existing Metal–ligand coordinations are not the reason in fixing and releasing the temporary shape, instead having the transition of elastic to rubbery state in vicinity of cold crystallization temperature in semi-crystalline polymer provides HKUST-1 to act as a physical cross linking or netpoints. Moreover, the reinforcement accompanied by increased toughness resulting from HKUST-1 offering a great combination of features which demonstrates the fact that how exciting features can be obtained with simply using a piece of reticular chemistry.

CP06.04.24

Optically Switchable Photoelectron Injection from Perovskite Nanorods for Wavelength-Distinguishable UV Photodetector

Due to their hybrid inorganic–organic nature, MOFs possess attractive characteristics that are absent from purely inorganic or organic systems, the organic parts allow them to interact chemically with polymeric chains to ensure chemical nucleation. Moreover, MOFs can exhibit, for example, higher surface areas while maintaining a degree of mechanical flexibility that is largely inaccessible to inorganic materials which can lead to enhanced nucleation of small polymer crystals.

Ultrafast (UV) radiation has given rise to high-speed, wide-cover and non-line-of-site wireless optical communications due to its small susceptibility to solar background interference and flexibility of transmitter/receiver orientations such as pointing, acquisition and tracking. For a wireless UV communication, function generator produces pattern-controlled electrical signals that contain characteristic information on the intensity and on-off frequency of UV lights, which are emitted by transmitter and subsequently detected by receiver to realize the relay of information. Moreover, UV radiations with different wavelengths are employed in communication systems so as to enable bidirectional and high-capacity optical transmission, where large distinction between UV wavelengths is demanded for minimized inter-channel interference. Therefore, developing a photodetector that can accurately identify UV intensity variation, while simultaneously distinguishing UV photons in different wavelengths is highly desirable for acquiring and decoding the information embedded in UV carriers. Owing to the suitable bandgaps and superior charge transport properties, lead halide perovskites (e.g. MAPbCl\(_3\), CsPbCl\(_3\), FAPbI\(_3\)) have realized high-performance UV photodetectors. Nonetheless, such photodetectors were never able to differentiate UV photons with different energies due to indiscriminate, unidirectional transport of photogenerated charge carriers in 1) prototypical p-i-n photodiode structures, 2) lateral photoconductor structures with external voltage biases, and 3) devices utilizing metal electrodes with much discrepant work functions for guided carrier migration. In addition, photodetectors need to be sufficiently sensitive to accurately detect UV photons with temporally varying flux based on superior photoelectronic properties (e.g. large free carrier density, high mobility), since optical information can also be ciphered in the oscillating intensities. As such, it is intriguing both at scientific and technological levels to develop UV photodetector that permits multidirectional carrier transport in perovskite materials with radically improved optoelectronic properties, so as to observe perturbed photocurrent responses and to eventually elucidate the energies and intensities of UV photons. Here, with the presence of LiCl additive in formamidinium chloride (FACI) solution, as-grown LiCl:FAPbCl\(_3\) nanorods demonstrated greatly enhanced crystallinity and UV photoresponse as compared to pristine FAPbCl\(_3\) nonastructure without LiCl additive. Most importantly, LiCl:FAPbCl\(_3\) nanorod film exhibits unprecedented distinguishability to UV lights with different energies and oscillating intensities, via unpolar/bipolar and periodically oscillating photocurrents. This work could advance the fundamental understanding of photoinduced carrier processes in halide perovskites and facilitate the development of novel UV-based optical communications.
piezoelectric materials with better properties. More recently, within the context of microscale devices such as Smart MEMS, self-powered sensors, microbatteries, and energy harvesting devices, there is a growing interest in developing “thin-film” piezoelectric materials. While, advances in microfabrication technology have greatly helped the synthesis and fabrication of piezoelectric thin films and structures, there is a continuing need to develop small-scale test methods to characterize the properties of such thin film piezoelectric materials. While nano-indentation-based methods of property determination have been demonstrated to provide useful information about the mechanical properties – elastic, plastic, hard, and fracture properties, of metallic materials in the thin film form, relatively fewer efforts have focused on developing the nanoindentation (or indentation) technique for understanding the electromechanical properties of thin-film piezoelectric materials.

The objectives of the present work are: (i) to obtain a comprehensive understanding of the indentation response of several classes of anisotropic piezoelectric materials; (ii) to elucidate the role of the indenter geometry and the indenter conductivity on the effective indentation response of anisotropic piezoelectric materials; (iii) to characterize the effects of electric fields on the indentation response of piezoelectric materials; (iv) to compare the indentation response of piezoelectric thin films with that of piezoelectric islands; (v) to differentiate between materials that are piezoelectrically active or passive, that is, polarized and unpoled, and those that are piezoelectrically strong and weak; and (vi) to identify the principal poling directions in active materials.

Three-dimensional finite element models are developed to accurately capture the force–depth and charge–depth nanoindentation response of several classes of anisotropic piezoelectric materials such as relaxor ferroelectrics for which analytical models are at present unavailable. Upon validating the finite element model for transversely isotropic materials and with experimental results, it is demonstrated that the nanoindentation response of anisotropic piezoelectric materials displays a strong dependence on the nature of the indenter geometry and relatively weak dependence on the indenter conductivity. Furthermore, by recourse to “longitudinal” and “transverse” indentations, the nanoindentation method can also be used to identify the poling directions in piezoelectric materials as well. It is also demonstrated that the indentation of piezoelectric materials which are subjected to electric fields can be used to uniquely identify the piezoelectric characteristics of thin films that exhibit in-plane poling as well.

Flexible and Light Weight CNT/Silk Foam for Strain Sensor with Superior Compressibility and Sensitivity

Flexible strain sensors have attracted attention in recent years for applications in diverse field starting from soft robotics to human-machine interfaces and wearable health monitoring devices. We engineered a novel, lightweight, flexible, porous architecture composed of carbon nanotubes (CNT) and silk which act as strain sensor. Such structures were fabricated using simple salt-leaching technique where the foam densities were varied from 0.06 to 0.14 gm cm$^{-3}$ by altering CNT and salt contents which eventually tunes the
porosity of the structure up to 60%. The study showed that during compression, cell wall of the foams start moving towards each other reducing the gap between cells and form new conduction path and hence the resistance of the structure reduces along the compression direction with the increasing strain. At 50% compressive strain the normalized stress of CNT/silk-based foams structures were ranged from 30 to 60 MPa gm cm
-2. The relative change in resistance of the structures with increasing strain (up to 50% strain) follows a linear characteristic which provides an additional advantage for its application as piezoresistive strain sensor. The foam with highest porosity (60% porosity) and lowest electrical conductivity showed extremely high piezoresistive sensitivity with tuneable gauge factor ~ 250% at 50% strain. The study also revealed that with the increase in CNT content, electrical conductivity increases whereas the gauge factor decreases. For compression over multiple cycles (> 200 cycles) the foam structures exhibited excellent stability and reversibility in terms of stress and resistance. The tuneable piezoresistive sensitivity and conductivity of the structures make them suitable candidate for the application as strain sensor in the field of soft robotics, flexible and wearable electronics etc.

10:45 AM CP06.05.07
High Energy Density Capabilities of Relaxor-Ferroelectric Thin Films Using Interlayer Coupling
Amrit Sharma, Bo Xiao, Sangram K. Pradhan and Messaoud Bahoua; Materials Science, Norfolk State University, Norfolk, Virginia, United States.

Relaxor-ferroelectric multilayer heterostructure provides a high electric displacement or charge density, a large area to store the energy and fast discharge capacity. We have grown lead-free BaZr0.2Ti0.2O3 (BZT)/BaCa2−xTixO3 (BCT) multilayer heterostructures and studied the structural, dielectric, ferroelectric and energy density characteristics. The BZT/BCT multilayer epitaxial heterostructures were grown on La0.68Sr0.32MnO3 (LSMO) buffered SrTiO3 (STO) single crystal substrate by optimized pulsed laser deposition parameters such as substrate temperature, oxygen pressure and film thickness. The large angle x-ray scans showed only diffraction peaks from the substrate and pseudocubic reflections (00l) from the multilayer heterostructure, confirming that these films are phase pure and epitaxial in nature. The atomic force microscopy (AFM) studies indicate that the surface roughness is low and that film growth is of high quality. The low leakage current confirms the films are highly insulating in nature which is the basic requirement for the dielectric energy storage. The ferroelectric phase transitions have been proved above room temperature with relaxor behavior. The polarization versus electric field (P-E) measurement exhibits single and well-saturated hysteresis loop with large polarization. The enhancement in polarization is due to a combination of space charge effect and interlayer charge coupling between two neighboring layers. Our lead-free relaxor-ferroelectric multilayer heterostructures exhibit good energy densities with better performance at low voltage above the room temperature which will be of great interest for researchers working on the physics and materials science.

11:00 AM CP06.05.08
Investigation of Electrical, Dielectric and Ferroelectric Properties of Lead-Free K

Na

1-x

3

NbO

3

Thin Films Near the Morphotropic Phase Boundary
Shweta Sharma1, Ashok Kumar2, Vinay Gupta3, Monika Tomar1 and Surbhi Gupta1; 1Physics and Astrophysics, University of Delhi, Delhi, India; 2Department of Physics, University of Delhi, Delhi, India; 3CSIR-National Physical Laboratory, Delhi, India.

Lead-free Potassium Sodium Niobate (K

Na

1-x

3

NbO

3

or KNN) has gained humungous popularity in the recent years due to increased environmental concerns and measures taken towards restraining the dominant use of toxic lead-based materials such as PZT in sensors and actuators for industrial applications. KNN, being eco-friendly, is considered to be a potential replacement to PZT due to its high Curie temperature (\(\sim 400^\circ\text{C}\)) providing broad temperature range for operation, and high piezoelectric and ferroelectric properties. As per the reports, a ferroelectric material exhibits the optimum electrical and piezoelectric properties at compositions especially near their morphotropic phase boundaries, where two ferroelectric phases are believed to co-exist. In K

Na

1-x

3

NbO

3

there exist three morphotropic phase boundaries (MPB) at x=0.17, x=0.35 and x=0.50 where the properties appear to be optimum. Although there are reports in literature on the KNN based ceramics, there is no report so far on the comparative study of the properties of K

Na

1-x

3

NbO

3

thin films at composition near MPB. Attaining of the high dielectric and ferroelectric properties of KNN based thin films is significant for the realization of lead-free microwave-based devices for use in high frequency applications.

The present work investigates the electrical, dielectric and ferroelectric properties of K

Na

1-x

3

NbO

3

thin films near morphotropic phase boundaries [at compositions; KNN-35 (x=0.35) and KNN-50 (x=0.50)]. The KNN thin films have been deposited using pulsed laser deposition (PLD) technique at optimized parameters. The dielectric properties and conductive behavior of the KNN-35 and KNN-50 thin films have been investigated and compared in a broad temperature range. The ferroelectric nature of the KNN-35 and KNN-50 thin films were confirmed by the obtained saturated Polarization-Electric field (P-E) hysteresis loops. The obtained results of the dielectric constant and remnant polarization for both KNN-35 and KNN-50 are promising for the integration of K

Na

1-x

3

NbO

3

thin films in MEMS based microwave tunable devices.

11:15 AM CP06.05.09
Dual Ion Beam Sputtered RRAMs Exhibiting Quantum Conductance
Armitesh Kumar, Mangal Das, Sanjay Kumar, Vivek Garg, Md Arif Khan, Abhinav Kranti and Shabdal Mukherjee; Indian Institute of Technology Indore, Indore, India.

We report forming-free (FF) resistive random access memory (RRAM) with high endurance and retention for ZnO based thin films fabricated by dual ion beam sputtering (DIBS). We report the effect of interface anomalies such as disorder-induced interface states, Schottky barrier formation/dissolution for a resistive switch or memristor. Distribution of bulk defects with applied bias governs switching and also attributes to formation/dissolution of interfacial oxide. Further, conductance quantization is observed in the device. Device shows excellent endurance and retention with forming-free behavior. Besides, conductive quantization as exhibited by device can be used to further work upon synaptic properties of device. The present work considerably contributes to further understand the conduction mechanisms of a wide range of resistive switches.

11:30 AM CP06.05.10
Micro-Plasma Based Enhancement in Dielectric and Piezoelectric Properties of ZnO Based Multifunctional Composite Thin Films by Surface Modification—Towards Applications in Touch Based Sensors and Wearable Devices
Siddharth Mageshkumar1, Harlavpreet Brar2, Mia Bentzen2, Walker Tuft1, Saqib Ahmed2 and Sonika Baniaerjee1; 1Mechanical Engineering, California State University, Fresno, Fresno, California, United States; 2Mechanical Engineering, Buffalo State College, Buffalo, New York, United States.

Atmospheric pressure and ambient temperature based micro-plasmas have been used in polarization and alignment of dipoles in ferroelectrics. The same phenomenon can be used to enhance the surface energy and surface characteristics of composite multifunctional thin films by means of surface modification. A significant increase in non-thermal atmospheric plasma applications, such as dielectric barrier discharge (DBD) and corona discharge plasmas have been steadily increasing in industry and in the research literature. The current work involves the use of corona micro-discharge for surface modification of ZnO/ZrO nanowire-Epoxy-Graphene based multi-functional and flexible thin film devices towards enhancement in surface bonding characteristics and variation in surface wettability and surface energy characteristics. The parameters being investigated in the experiments include plasma device characteristics such as voltage, current, and frequency, as well as other significant parameters such as displacement between thin film and DBD/Corona discharge source, treatment time, and temperature of the plasma. The modified surface micro-structure is analyzed using a scanning electron microscope, profilometry, impedance spectroscopy and the bulk electrical, dielectric, and piezoelectric properties are characterized using impedance spectroscopy and piezoelectric strain coefficient measurements.
continuously being proposed and executed to reverse the trends of obesity prevalence. These efforts are often led by non-profit organizations, school administrator, university researchers, state agencies as well as federal agencies. For a long time the monitoring tool available to the population at large has been the low-cost weighing scale and only recently, as wearable electronics are becoming more widespread, new tools such as step and calorie counters are becoming available but remain expensive. This work provides insights on how novel breath-gas sensors and skin wearable sensor nanotechnology may be used for monitoring the metabolic rate patterns of individuals in relation to their diet and exercise activities. It also addresses the need for human-computer interface systems that treat social network-based support groups as learning organizations. The latter can interface with the metabolic rate monitors to effectively promote positive health behavior. The synergy of the two technologies is expected to revolutionize personalized medicine and to radically improve health and well-being practices.

2:00 PM CP06.06.02
Hybrid Wearable Devices for Non-Invasive Real-Time Monitoring of Blood Glucose—Optimization of Process Parameters by Analysis of Data Sets from Impedance Spectroscopy and Photoacoustic Measurements Aided with Artificial Intelligence

Chaitanya Sreenivas¹, Mohamed Muthana¹, Jodi Bishop², Soumyasanta Lahaj¹, Shaestagir Chowdhury¹, Saquib Ahmed¹ and Sankha Banerjee¹; ¹Mechanical Engineering, California State University, Fresno, Fresno, California, United States; ²Electrical and Computer Engineering, California State University, Los Angeles, Los Angeles, United States; ³Mechanical Engineering, Portland State University, Portland, Oregon, United States; 4Mechanical Engineering, Buffalo State College, Buffalo, New York, United States.

Diabetes is a chronic disease that affects a large part of the population in the United States and around the world. Real-time monitoring of blood glucose can detect early signs of diabetes by diagnosis conditions such as impaired glucose tolerance. A wide range of analytical methods and techniques are being studied for non-invasive and real-time testing/monitoring of blood glucose. These techniques include Optical Spectroscopy, Raman Spectroscopy, Photoacoustic Spectroscopy, Impedance Spectroscopy and Microwave based measurement methods among others. The following work deals with the analysis of a proof of concept hybrid monitoring system using a combination of optical and non-optical techniques such as Photoacoustic Spectroscopy and Impedance Spectroscopy. Data sets from the two methods are analyzed base on process parameters such as optical absorption, thermal expansion, acoustic velocity, specific heat, dielectric, and impedance characteristics. A system architecture based on multi-sensor and multivariable optimization is proposed. Further, to make it adaptive to different practical situations, AI or machine learning algorithms are to be investigated and implemented for reliability.

2:15 PM CP06.06.03
Development of Breathable, Self-Sealing Hazmat Suit Material for Chemically Hazardous Environments Kenneth C. Manning¹, Akshay Phadnis¹, Timothy P. Burgin² and Konrad Rykaczewski¹; ¹School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; ²School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States.

The impermeability of current hazmat suits restricts the thermoregulation of the user by blocking the water vapor, which can be fatal when used over a relatively short period of time (~30 minutes) in absence of auxiliary cooling systems. Here, we develop a smart hazmat suit material based off stimuli responsive polymers that selectively swell upon action of hazardous chemical aerosols. Specifically, we develop a breathable, composite fabric that allows for perspiration cooling until they are exposed to a target range of hazardous chemicals. Once exposed, the polymer rapidly swells to close pores in the fabric turning into an impermeable membrane. Consequently, thermal stresses on the user are minimized by occurring only during actual exposure to hazardous materials. To achieve this, we develop a selectively swelling polymer, poly(N,N-butylenediamine), and integrate it with typical fabrics used in MOPP gear to create the adaptive, smart composite materials. We demonstrate the selective permeability of this smart composite fabric through a series of vapor transmission and droplet impingement experiments where we show that the fabric is permeable to water vapor but blocks droplets of target chemicals by swelling. We quantify the efficacy of this fabric in terms of response time and chemical containment. The response time largely depends upon the chemical permeation properties and polymer particle size/shape and varies inversely with it. Additionally, we develop a high-fidelity numerical model to capture the transient dynamics and optimize the polymer shape and size. Specifically, we develop a finite element model to describe aerosol droplet-polymer interactions and polymer swelling kinematics. This model is based on implementation of concurrent fluid permeation and large deformation theory combined with constitutive relation based on Flory-Rehner theory. In combination with the experimental data, we use this model to optimize the fabric design for maximum breathability while retaining the required protection levels for the user.

References:

2:30 PM BREAK

SESSION CP06.07: Smart Systems inspired by Biology
Session Chairs: Krishna Challagulla and P.I. Gouma
Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 105 C

3:30 PM CP06.07.01
Bioinspirational Principles for Design of Smart Biointerfaces for Regenerative Medicine and Cancer Metastasis Models Kahtana Katti1, 2, 3, Sumanta Kar1, 2, 3, MD Shahjahman Molla1, 2, 3, and Dinesh R. Katti1, 2, 3; 1Civil and Environmental Engineering, North Dakota State University, Fargo, North Dakota, United States; 2Center for Engineered Cancer Testbeds, North Dakota State University, Fargo, North Dakota, United States; 3Materials and Nanotechnology, Biomedical Engineering, North Dakota State University, Fargo, North Dakota, United States.

Biointerfaces of biological and engineered surfaces are relevant for many applications in biomedical, energy and structural applications. Tissue engineering is a promising technology for regenerating tissues and organs. The degrading scaffold in close molecular proximity of growing tissues represents a dynamic and intelligent interface that is controlled by genetic characteristics of cells as well as the physical and chemical characteristics of degrading scaffolds. We describe the use of a biomimetic mineralization process of mineralizing hydroxyapatite inside amino acid modified nanoclay for design of biomimetic and smart scaffolds for bone tissue engineering. The nanoclay scaffold enables growth proliferation and differentiation of human mesenchymal stem cells to generate tissue engineered bone with structural hierarchy characteristic of human bone, as well as the Ca/P stoichiometry characteristic of new amelodonic bone. This type of bone is typically the niche to which prostate and breast cancer cells migrate to from their original location in a process called metastasis. At this point of bone metastasis, the prognosis is usually dismal for the patients and metastasis is the cause for most cancer deaths. We report the use of the smart scaffold to generate the first in vitro model of human prostate and breast cancer bone metastasis. The tumors at the metastasis site are investigated for gene expression that indicates that indeed the cancer is in late stage metastasis (also known as the mesenchymal to epithelial transition or MET). We report the use of FTIR and nanomechanics to capture disease progression at metastasis. The significance of the use of the scaffolds as cancer testbeds lies in the fact that human samples are unavailable and animal models fail, due to death of animal before metastasis to bone. Engineered biointerfaces of the smart scaffolds are thus the key to development of therapies advanced stages of metastasis.

4:00 PM CP06.07.02
Bioinspired Design Strategies for Nanostructured Materials Mingsheng Dua1, 2; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2School of Biological Sciences, Nanyang Technological University, Singapore, Singapore.

Reducing microstructure dimensions down to the nanoscale can significantly improve the material strength. However, this is often accompanied by lower ductility, reduced fracture toughness and/or smaller fatigue crack growth resistance. There have been a number of successful strategies for achieving all-around superior mechanical properties, including the introduction of growth or deformation nanotwins, microstructure/nanostructure gradation, and various bioinspired strategies. Here a number of bioinspired nanostructure design strategies are proposed and discussed. One particular strategy is inspired by the exceptionally strong and ductile structure of byssal threads found in certain mussels. The excellent mechanical properties are shown to be
realized by structurally introducing sandwich structures at both the macro- and nano-scales. On the other hand, nanoscale heterogeneity of bone has been identified to enhance inelastic energy dissipation. Experiments and simulations have been carried out to quantify the size-dependent heterogeneity, and understand the relative importance of elastic and inelastic heterogeneity. Parameters that affect energy dissipation are investigated under typical deformation modes of bone, and possible routes to enhance this effect are discussed. Additional bioinspired microstructural design strategies are also discussed, including geometrically interlocking interface for enhanced strength as well as elastically mismatching surface layers for delayed catastrophic structure failure.

Additional safety factors for delayed catastrophic structure failure.

4:15 PM CP06.07.03
Electrochemically-Driven Transport for Room-Temperature Healing of Metallic Cellular Materials with Synthetic Vascular Systems

Numerous biological materials regenerate and self-heal in response to damage which allows them to strengthen areas under high mechanical stress and maintain their load-bearing capabilities for many decades. In bone, self-healing is enabled by the transport of nutrients and minerals through a vascular system embedded within a load-bearing cellular structure. In contrast, most human-made structural materials cannot autonomously heal or tune their mechanical strength. As a result, structures are designed with safety factors so that the strength of their constitutive materials is well above any stress they are expected to endure. Hence, not only are most human-made structures heavier and more voluminous than strictly necessary, but they also require regular monitoring and maintenance to guard against fatigue cracking, particularly in critical applications (aerospace vehicles and power plants, for example).

Self-healing materials have been developed to overcome the deficiencies of structural materials, but mostly rely on a “local healing” approach where the healing agent is available throughout the material so that cracks heal using material in the crack vicinity. Although successfully demonstrated in polymers, this method has proven impractical in metals without the external provision of heat, since metal atoms possess low diffusivities near room temperature.

Here, we overcome these limitations and report, for the first time, rapid and effective self-healing of metallic cellular materials at room temperature using electrochemistry as a method, and the structure of bones and their self-healing processes as an inspiration. In contrast to previous techniques, electrochemically-driven healing relies on the transport of metal as an ion through an electrolyte, which allows faster transport, as metal ion diffusivities in a room temperature electrolyte (~10^{-5} m^2/s) are at least three orders of magnitude greater than metal atom diffusivities in a room temperature solid. Consequently, our self-healing technique uses at least three orders of magnitude less energy to heal a crack of a given length compared to techniques which rely on heat-driven diffusion or precipitation in metallic alloys. We use tensile testing of dog-bone shaped open-cell nickel foams coated with a passivating layer, followed by electrochemical healing to understand the relationship between material structure and healing capabilities. Our nickel open-cell foams show full recovery of tensile strength and toughness using an external nickel source during healing. The use of a passivating polymer coating on the nickel foams improves the probability of achieving full recovery of tensile strength compared to uncoated nickel foams. Moreover, we show that by varying the maximum strain of the passivating coating, self-healing metals with three distinct functionalities can be achieved: materials that increase their local stiffness before failure, materials that heal microscale cracks and materials that only heal macroscale cracks above a threshold size. Finally, we design a nickel foam composite which uses an electrolyte embedded within a internal synthetic vascular system to redistribute load-bearing nickel to damaged areas and recover lost mechanical strength. Pathways for enabling a truly autonomous self-healing metallic material are discussed.

4:30 PM CP06.07.04
Catalytic Mechanism of Biomaterials in Cartilage—A Bottom-Up Computational Investigation of the Aggrecan Cleavage Site
Deng Li and Shu-Wei Chang; Department of Civil Engineering, National Taiwan University, Taipei, Taiwan.

Cartilage is an important smart material which provides crucial mechanical properties for our body. Many diseases are associated with abnormal aggrecan degradation in articular cartilage. Aggrecan degradations are mainly controlled by matrix metalloproteinase-8 (MMP9). MMP8 cleaves at the catalytic cleavage site of Glu373-374Ala in the aggrecan core protein, with another potential cleavage site at Glu419-420Ala, however, left uncut. The catalytic mechanism of how the MMP8 recognizes the catalytic cleavage site has not yet been revealed. Understanding how nature design materials to be degraded at only specific regions can enable the design of new synthetic smart materials for many engineering applications.

To investigate this, we use a bottom-up computational mechanics approach to explore this conundrum. We found that the two key residues in the vicinity of the catalytic site, arginine in P2' and glycine in P3' play an important role in forming a stable binding pose of MMP8-Actual_peptide complex. For the potential cleavage site, the arginine is replaced with Threonine and the glycine is replaced with arginine, resulting in the unstable binding pose of MMP8-Potential_peptide complex. Our results suggest that MMP8 is able to recognize the molecular structure of the catalytic cleavage site and only cleave Glu373-374Ala in the aggrecan core protein. By calculating the binding affinity between MMP8 and aggrecan core protein, we find that the binding energy of MMP8-Actual_peptide complex is higher than the binding energy of MMP8-Potential_peptide complex. We hypothesize that the stable binding structure of the catalytic cleavage site of aggrecan core protein makes MMP8 stay in an “active” state, and then hydrolyze the scissile bond of aggrecan core protein. On the contrary, unstable binding between the potential cleavage site of aggrecan core protein and MMP8 makes MMP8 stay in an “inactive” state. Our results provide fundamental insights into the catalytic mechanism of biomaterials in cartilage at the molecular and nanoscale level.

4:45 PM CP06.07.05
Contribution of Biomimetics and Simulation to the Development of 4D Printed Hydrogels
Daniela Ribeiro and Silvia L. Titotto; CECS, Universidade Federal do ABC, Santo André, Brazil.

Cartilage problems are becoming more frequent due to some factors such as population aging. Using biomimetics to understand how to minimize this problem, a biomaterial very sensitive to external stimuli has been studied as a possible substitute for worn cartilages: hydrogel, a biocompatible polymer. Thus, in order to create a basis for the feasibility of the application of this material, it is necessary to know different types of hydrogels, for instance, Poly (acrylic acid) and Polyethylene glycol, and to understand how they behave under external variations, such as pH and temperature. Accordingly, the work presented was based on recent bibliographical studies accessed mainly via Science Direct, Scientific Reports and Research Gate, for collecting fundamental information of this subject with the objective of producing visual simulation results via SolidWorks / Flow Simulation. Furthermore, the work will present objects composed of hydrogel printed in different formats by an experimental 4D printer developed at Federal University of ABC in collaboration with our research group 4DB. Moreover, it will be demonstrated how those printed objects behave in relation to external stimuli. It is hoped that the dissemination of the partial results of this ongoing research will contribute to the advancement of the subject in the interdisciplinary scientific community.

SESSION CP06.08: Smart Approaches to Modeling and Simulation
Session Chairs: Shou-Yi Chang and T. Venkatesh
Thursday Morning, April 25, 2019
PCC West, 100 Level, Room 105 C

8:30 AM CP06.08.01
A Multiscale Modelling Strategy to Predict Precipitate Stability, Nucleation and Growth in Metallic Alloys
Hong Liu1, Ioannis Papadimitriou2, Bárbara Bellón2,1, F. X. Lin1 and Javier Llorca1; 1Technical University of Madrid, Madrid, Spain; 2IMDEA Materials Institute, Getafe, Madrid, Spain; 3KU Leuven, Leuven, Belgium; 4UC Louvain, Louvain, Belgium.

Precipitation hardening is one of the most efficient mechanisms to increase the yield strength of metallic alloys but accurate quantitative models to predict the size, shape and spatial distribution of precipitates during high temperature ageing are still lacking. In this presentation, a multiscale modelling strategy is presented to determine the precipitate stability as a function of temperature, the process of homogeneous and heterogeneous nucleation and growth of precipitates. Precipitate stability is assessed from the calculation of
the free formation energy obtained from first principles calculations of the formation enthalpy at 0K together with the vibrational entropy contribution. Homogeneous and heterogeneous (on dislocations or other precipitates) precipitate nucleation is analysed by means of classical nucleation theory in which the different contributions to the Gibbs free energy (chemical interfacial and elastic) are determined from computational thermodynamics, first principles calculations and geometric considerations of the lattice distortion, respectively. Finally, precipitate growth up to the equilibrium shape was also determined by means of mesoscopic phase-field model.

The strategy was applied to analyse precipitation in Al-Cu alloys at high temperature, a regime in which three different kinds of precipitates can be found (8º, 9º and 0º). The results of the multiscale modelling strategy were in good agreement with the experimental data and it is envisaged that the strategy presented in this investigation can be used in the future to design optimum microstructures based on the information of the different energy contributions obtained from first principles calculations.

9:00 AM CP06.08.02

The fundamental understanding of the structure – property relationships of SMART materials at the atomistic level is a critical step towards rational design for targeted applications. On the experimental side, X-ray absorption spectroscopy (XAS) is a premier element-specific technique for materials characterization. Specifically, X-ray absorption near edge structure (XANES) carries rich local structural and chemical information around X-ray absorbing species, which makes it a powerful tool to probe materials structure and dynamic processes. As such, unraveling the local chemical environment from XAS spectra is akin to solving a challenging inverse problem. Because the structure - spectrum relationship is obscure, solving the inverse problem often requires prior empirical knowledge, which is qualitative or semi-quantitative and not transferable. Here we show how data science can be combined with first-principles theory to decipher the structure-spectrum relationship from XANES, with only a small amount of experimental data typically available for training. Such an approach can be applied in multiple contexts, including prediction of the 3D structures of metal nanoparticles using machine learning, local structure refinement of amorphous materials from a XANES database, and local chemical environment classification using XANES database and machine learning methods.

9:30 AM CP06.08.03
First-Principles Study of Doping Effects on Transformation Temperatures in Ni-Mn-Ga Magnetic Shape Memory Alloys Martin Zelený 1, 2, Jozef Janovec 1, Alexei Sozinov 1, Ladislav Straka 1, Torbjørn Björkman 2, Risto M. Nieminen 2 and Oleg Heezho 1, 2; 1 Institute of Physics of Charles University, Faculty of Mathematics and Physics, Charles University, Prague, Czechia; 2 Institute of Materials Science and Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czechia; 3 Material Physics Laboratory, Lappeenranta University of Technology, Savonlinna, Finland; 4 Institute of Physics, Czech Academy of Sciences, Prague, Czechia; 5 Physics/Department of Natural Sciences, Åbo Akademi University, Turku, Finland; 6 COMP/Department of Applied Physics, Aalto University School of Science, Aalto, Finland.

The influence of Co, Cu, Zn and Cd doping on Ni-Mn-Ga Heusler alloy exhibiting magnetic shape memory behavior is investigated using the first-principles exact muffin-tin orbital method in combination with the coherent potential approximation. The control of material properties relative to structural and magnetic phase transitions, especially martensitic transformation temperature $T_M$ and Curie temperature $T_C$, is important for potential engineering applications in actuators, sensors, vibrational energy harvesters, or magnetic refrigeration systems. The energy difference between the austenite and the nonmodulated martensite phase $\Delta E_{AM}$ obtained from first-principles calculations can be used as a qualitative indicator of $T_M$ whereas the energy difference between paramagnetic and ferromagnetic state $\Delta E_{PM-FM}$ serves for prediction of $T_C$. In addition, reducing of equilibrium tetragonality of nonmodulated martensite $(c/a)_{NM}$ allows higher mobility of martensitic twins due to lower twinning stress, which further improve magnetic shape memory properties.

For Cu doping of a Ga-deficient alloy, we have found a strong increase in $\Delta E_{AM}$ but just a small change of equilibrium $(c/a)_{NM} = \Delta E_{PM-FM}$ decreases in martensite phase and remains almost unchanged in austenite phase. If, on the other hand, Cu is instead doped at Mn sites, the increase of $\Delta E_{AM}$ is much smaller and a slight decrease of $(c/a)_{NM}$ is seen. $\Delta E_{PM-FM}$ strongly decreases in both phases with increasing concentration of Cu. Co doping at Ni sites has much stronger effects, with increasing concentration of Co strongly decreasing both $\Delta E_{AM}$ and $(c/a)_{NM}$. These theoretical results are in good agreement with previous experimental findings that Cu doped in the Ga or Mn sublattice increases the martensitic transformation temperature $T_M$ and Co in the Ni sublattice decreases it. Our results for Cu and Co doping also correspond to an empirical rule that $T_M$ is correlated with the number of valence electrons per atom, $\bar{a}$, in the alloy. According to this rule Zn and Cd with more valence electron than Cu should provide stronger increase of $T_M$ as well as $\Delta E_{AM}$ if these elements are used for doping instead of Ga or Mn. However, our results show that doping Zn or Cd in Ga-sublattice will results in the increase of $T_M$ but weaker compared to Cu doping. $T_C$ seems to be affected only weakly. The substitution of Mn atoms causes the decrease of both $T_M$ and $T_C$. Thus, in contrast to Cu doping the calculation did not support the validity of the $T_M \sim \bar{a}$ rule for Zn and Cd doping.

We have also investigated alloys where both elements Cu and Co were used in simultaneous doping. Our results show that the effects of simultaneous doping can be estimated using a linear superposition of the effects of individual dopants. This can be used for effective tuning of material properties; in particular, the decreasing of $\Delta E_{AM}$ (and $T_M$) arising from Co doping can be compensated by Cu doping at Ga sites. Moreover, the reduction of $(c/a)_{NM}$ due to the Co doping is preserved because the Cu doping has just a small effect on this quantity.

9:45 AM CP06.08.04
Analysis of Conducting Filaments in HfO2 Memristors Darshan G. Pahinkar and Samuel Graham; Georgia Institute of Technology, Atlanta, Georgia, United States.

Field effect transistors (FETs) with their Boolean operation have been the fundamental building block of digital computers. While this digital framework is excellent at performing complex arithmetic and logic calculations, it lags far behind the human brain in key areas such as adaptivity, generalization, and pattern recognition. Furthermore, as the size of these transistors is reduced, energy consumption and heat removal become a critical issue. Therefore, alternative technology initiatives such as analog switching are being explored. Neuromorphic computing using nanoscale adaptive oxide devices or memristors is a very promising alternative to this framework. Oxides of transition metals such as hafnium (HfO2) are proven to be excellent candidate materials for these devices, which show non-volatile memory and analog switching, while using only two terminals, instead of three as in case of standard FETs. These devices are simple in terms of arrangement, wherein a few nanometers thick HfO2 and an Hf metal layer are deposited between two electrodes on a substrate.

The naturally occurring HfO2 has insulating properties. When it is applied with a voltage bias, Hf and O atoms dissociate, creating positively charged oxygen vacancies. While negatively charged oxygen ions migrate toward positively charged electrode and are temporarily stored in the adjacent pure Hf layer, a conducting filament of positively charged vacancies forms, which facilitates the flow of electrons through it. This is known as the on-state of the device or ‘set stage’. When the polarity reverses, oxygen ions move back into the oxide layers neutralizing the positively charged vacancies, thereby gradually creating insulating layers of HfO2. As these layers are created, current flow through the device is drastically reduced and eventually an off-state is said to have occurred. This suppression of conducting filament is known as the reset stage. The extent of set/reset through applying alternate positive/negative voltage is temperature dependent transient process and is not completely characterized. Comprehensive understanding of coupled electrical current, ion/vacancy movement and heat transfer is essential to achieve the reliable and repeatable analog switching of this material.

This work focuses on the computational and experimental investigation of local and temporal variation of voltage, current and temperature, so that the coupled nature of heat transfer and current flow through these devices could be analyzed. By simulating the coupled heat transfer, current flow and vacancy/ion movement in COMSOL Multiphysics, the effect of substrate thickness and materials, set/reset voltages on relative on-state/off-state resistances, current magnitude and filament temperature is determined. Simultaneously, temperature of these devices is measured as a function of current and voltage using Micron capable transient temperature imaging (TTI) technique. The data from these experiments are used to develop useful information about the internal states of the devices. When the model results in terms of temperature and current history match well with those from the experiments, the COMSOL models are validated. Overall, coupled electrical current and heat transfer modeling and simultaneous measurements of current, voltage and temperature are expected to provide insightful information on switching mechanisms of these adaptive oxides and warrant their scaled-up implementation for neuromorphic computing.

10:00 AM BREAK
Three-Dimensional Strain Engineering in Epitaxial Vertically Aligned Nanocomposite Thin Films with Tunable Magnetotransport Properties

Xing Sun; Purdue University, West Lafayette, Indiana, United States.

A novel concept of integrating a three dimensional (3D) strain scheme in epitaxial thin films is present in this work by combining 2-phase vertically aligned nanocomposite (VAN) with thin interlayers for an effective coupling of the vertical and the lateral interface strain. This 3D strain scheme takes advantages of both architectures and promotes various strain-driven physical properties, e.g., record high magnetoresistance values (MR%) as low field magnetoresistance properties have been demonstrated in the LSMO-CeO2 interfingered with different numbers of CeO2 interlayers. This work brings a new approach to achieve highly strained films beyond the critical thickness in epitaxial thin films and to demonstrate enhanced vertical strain coupling by the 3D strain scheme. This demonstration not only shows the power of 3D strain scheme in strain engineering, multifunctionality coupling, and flexibility in structural designs, but also fulfills the urgent demands of new material designs for future electronic devices.


Single Nanoparticle Electrochromism Reveals Heterogeneous Coloration Rates and Ion Trapping Sites in Smart Windows

Justin Sambur and Russel C. Evans; Colorado State University, Fort Collins, Colorado, United States.

Developing large area electrochromic smart windows based on nanoscale materials demands that trillions of nanoparticles modulate between transparent and colored states at the same rate. However, it is unclear how nanoparticle heterogeneity contributes to variable coloration dynamics. Here we demonstrate a single nanoparticle electrochromism approach to study optical modulation rates upon lithiation of isolated, clustered, and thin film tungsten oxide nanorod electrodes. We observe a particle-dependent waiting time for coloration (from 100 ms to 1 s) due to Li-ion insertion at optically inactive surface sites. Longer nanorods achieve higher OD modulation than shorter nanorods because they develop a Li-ion gradient that increases from the nanorod ends to the middle. Interestingly, electrochromic irreversibility increases monotonically with the number of particle-interactions due to ion trapping at nanoparticle interfaces. These findings lead us to propose a nanostructured electrode architecture that optimizes coloration magnitude, rate, and reversibility across large area electrochromic smart windows.

Giant Magnetostriction and Low Loss in FeGa/NiFe Laminates for Strain-Mediated Multiferroic Micro-Antenna Applications

Kevin Fitzell; Joseph D. Schneider; JinZhao Hu; Zhi Yao; Collin R. Rementer; Nishanth Virshubados; Michelle Jamer; Cunzheng Dong; Anthony Barra; Daniel Gopman; Nian Sun; Julie Borchers; Brian Kirby; Yuanxun Wang; Rashanda Henderson; Abdon Sepulveda; Gregory Carman and Jane Chang; Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California, United States; Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California, California, United States; Electrical and Computer Engineering, University of California, Los Angeles, Los Angeles, California, United States; Electrical and Computer Engineering, University of California, Los Angeles, Los Angeles, California, United States; Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States; Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States; Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States; Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts, United States.

The ability to reduce the size of antenna elements would enable a revolution in wearable and implantable devices. Multiferroic antennae, composed of individual ferromagnetic and piezoelectric phases, are posed to reduce antenna size by up to 5 orders of magnitude through the efficient coupling of magnetization and electric polarization via strain. However, this strategy requires a low-loss magnetic material with strong magnetoelastic coupling at high frequency.

Galfenol (FeGaNi or FeGa) is a promising candidate material due to its large magnetostriction (>200 ppm), large piezomagnetic coefficient (>3 ppm/Oe), and high stiffness (>50 GPa), but it is highly lossy in the GHz regime. On the other hand, permalloy (Ni$_8$Fe$_2$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime (ferromagnetic resonance linewidth <20 Oe) but almost no magnetostriction. In this work, nanoscale laminates containing alternating layers of FeGa and NiFe were fabricated via DC magnetron sputtering to combine their complementary properties, yielding a small coercive field (<20 Oe), narrow FMR linewidth (<40 Oe), and high relative permeability (>700) (Rementer et al., 2017). These magnetic laminates were then grown on PMN-PT substrates and studied via polarized neutron reflectometry, demonstrating coherent rotation of the individual layers' magnetization with an applied electric field, supported by micromagnetic and finite element simulations (Jamer et al., 2018).

In addition, optical magnetostriction measurements confirmed the presence of greatly enhanced magnetostriction relative to single-phase FeGa; these laminates represent a threefold increase in magnetostriction at saturation (~700 ppm) and an enhanced sensitivity at low bias magnetic fields (25 ppm/Oe). This enhancement in magnetoelasticity relative to single-phase FeGa was correlated to the microstructure of these composites using TEM. Recent efforts have further enhanced the high-frequency properties of these composites through insertion of ultrathin Al$_2$O$_3$ layers to reduce the conductivity and mitigate eddy current losses, and subsequent integration of these laminates into a strain-multiferroic shear wave antenna successfully demonstrated the great potential of FeGa/NiFe laminates for use in microscale communications systems.

References:


Electric Field Control of Interfacial Magnetism Through Ionic Liquid Gating

Ziyao Zhou, Zhongqiang Hu and Ming Liu; Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi’an Jiaotong University, Xi’an, China.

Interfacial magnetism in magnetic heterostructures is of great significance for the applications in magnetic memory and microwave devices. Spin-polarized electric currents or magnetic fields have been the conventional driving forces to manipulate magnetic spin dynamics. A more energy-efficient alternative has been proposed in recent reports, where electric fields are used to manipulate magnetization in multiferroic heterostructures. Also, high-density charges aggregated at the interface of the ionic liquid can be used to manipulate the magnetic anisotropy, magnetoresistance, and metal-to-insulator transition in thin films, which are promising both in physics and applications. In this talk, we report electric field tuning of interfacial magnetization through ionic liquid gating in several magnetic material systems with in-plane or perpendicular magnetization anisotropy [1-4]. The spin dynamics of the multiferroic heterostructures during the ionic liquid gating process are monitored using in situ electron paramagnetic resonance (EPR), magneto-optic Kerr effect (MOKE), and vibrating-sample magnetometer (VSM) techniques. The electric-field modulation mechanisms, including ionic migration, electrostatic doping, and electrochemical reaction, are explored to realize non-volatile, reversible tuning and large magnetoelectric coupling coefficient. Our work on electric field control of interfacial magnetism may enable ultrafast, high-density, and power efficient spintronic devices.

References:


SESSION CP06.10: Processing and 3D Printing of Smart Materials
Session Chairs: Javier Llorca and Deyu Lu
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 105 C

1:45 PM CP06.10.02
Direct Writing of Amphiphilic Graphene Ink for Stretchable Tactile Sensors with Highly Sensitive and Ultra-Broadband Frequency Response Xin Jiang and Hongwei Zhu; Tsinghua University, Beijing, China.

Tactile sensors are essential for the next generation of sophisticated electrical devices including smart robotics, robot-assisted surgery, artificial skin and biomedical devices, etc. However, research on the detection of high frequency micro-vibration is still rare, because those tactile sensors should maintain ultra-high mechanosensitivity, high signal fidelity, conformal ability and fast response at the same time. Sensors that enable accurate sensing of sound frequencies are composed of precious metal or carbon/thermoplastic polymer composites. In this work, stretchable tactile sensors with highly sensitive and ultra-broadband frequency response are fabricated rapidly by direct writing amphiphilic graphene ink on plasma treated polydimethysiloxane (PDMS) film substrate. Due to the molecular interaction among graphene sheets/polypeptide, the composite conductive film on stretchable substrate produces cut-through cracks under the stress, and sheets do not undergo significant relative sliding action. This mechanical crack-based sensor has the characteristics of fast response and high sensitivity (with a gauge factor of 928.9 in the 0-2 percent strain range), and the gauge factor raises with the decrease of the resistance. Further, microscopic morphology of cracks, namely the crack asperity height and its statistical variance, can significantly affect the sensitivity and working strain range. We also demonstrate that sensors fabricated by direct writing can accurately detect the frequencies of different musical tones, chords and portaments. Moreover, diverse musical instruments could be recognized through the principal component analysis method. A general strategy for a green, simple, portable and cost-effective approach to make stretchable tactile sensors with highly sensitive and ultra-broadband frequency response is offered here, which could be widely applied in devices for detection of high frequency micro-vibration.

2:00 PM CP06.10.03
Fabrication of High-Performance Nanocomposites by Site-Specific Nanoparticle Orientation Through Additive Manufacturing Sayli Jambhulkar, Weiheng Xu, Rushik Tank and Kenan Song; Arizona State University, Tempe, Arizona, United States.

Nanoscale particles are widely used in various applications like drug delivery, wastewater purification and thermal management areas. However, its inability to manage their alignment during processing limits its widespread applications. This technique will focus on the printing of nanoparticles-containing composites via additive manufacturing process with the promoted local alignment of nanoparticles assisted by the surface morphology and fluidic flows. Specifically, nanoparticle orientation will be controlled within a unit printing volume to obtain suitable mechanical and functional properties. Projection micro-stereo lithography (PµSLA)/fine fiber spinning based fused deposition modeling (FFS-FDM) were used for building for 3D triangular wave shape surface pattern of PVA (poly vinyl alcohol) transparent polymer. The liquid crystal 4-Cyano-4'-pentylphenyl (5CB) and halloysite nanoparticles are diffused together and this mixture is deposited over the transparent pattern to study its alignment. 5CB liquid crystal provides sufficient driving force for the unidirectional alignment of halloysite nanoparticles. The factors like fluid dynamics, colloidal inks, solidification thermodynamics and confinement systems will control the nanoparticle configurations. The orientation of nanoparticles due to the alignment of nematic liquid crystal in the groove direction were studied by polarized optical microscopy (POM), atomic force microscopy (AFM), x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Mechanical properties like static modulus, strength and toughness were measured. The orientation management of nanoparticles will improve the efficiency of drug delivery, optical or electrical signal transfers and the robustness of automobiles etc.

2:15 PM CP06.10.04
Effective Unidirectional Wetting of Liquids on Biomimetic Patterned Surfaces via 3D Printing-Assisted Replication and Surface Modification Hau Che-Ni and Po-Yu Chen; Materials Science and Engineering, National Tsing Hua University, Hsinchu City, Taiwan.

Controlled self-propelling of liquid transport is of significant interest for extensive applications, such as DNA microarrays, fog-harvesting, self-cleaning coatings and smart microfluidic devices. It is found that many biological structures possess unique structural features that demonstrate unidirectional wetting behavior, such as cactus with conical spines, spider silk with periodic spindle-knots and joints, and Nepenthes peristome with overlapping grooves. Investigations on the structure-property-function relationships of
smart surfaces in Nature offer inspirations and insights into how to control the tendency of liquid self-transport without additional energy expenditure. In this work, we first applied the atmospheric pressure plasma (APP) treatment on inclined samples with a specific angle which resulted in gradient wettability and unidirectional wetting behavior was realized. To further improve the efficiency and durability, we further designed bio-inspired patterns consisting of arrays of asymmetric, spine-like structures and fabricated the negative molds by 3D-printing. Polydimethylsiloxane (PDMS) was utilized to replicate the bio-inspired patterns. Then, hydrophilic polyethylene glycol (PEG) was grafted onto the surface of PDMS replica in a two-step process, including APP treatment and liquid phase deposition. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) and profile and microstructure of PDMS replica were characterized by 3D laser scanning confocal microscopy and SEM, respectively. The static and dynamic wetting behavior of liquids on biomimetic patterned surfaces were evaluated and observed by contact angle measurement with varying tilting angles and high-speed camera. Results showed that the serial liquid droplets were unidirectionally driven by the asymmetric structure and gradient surface and were pinned in the opposite direction. The unidirectional wetting behavior of liquids was observed even when the tilting angle reached 90°. In summary, we successfully designed and synthesized biomimetic patterned surfaces by combining 3D printing-assisted replication, APP treatment and PEG grafting which possess effective unidirectional wettability and could be further applied in controlled fluid transportation, water/fog collection, microfluidic devices and smart textiles.

2:30 PM CP06.10.05
Solution Deposited Columnar Thin Films and Their Potential Application as Absorber Layers for SWIR Active Up-Conversion Devices Yuval Golan, Ben-Gurion University of the Negev, Beer Sheva, Israel.

Chemical solution deposition of lead chalcogenide thin films on GaAs substrates has been shown to result in a wide range of film microstructures, from ultra-thin nanocrystalline films, via highly oriented polycrystalline films, to single crystal films with epitaxial relation with the underlying substrate.[1-6] Of particular interest are columnar thin films, which are comprised of nanocolumn-which are vertically aligned with respect to the substrate. This talk will highlight the solution deposition route to columnar thin films, which are interestingly formed via an oriented attachment growth mechanism.[7] These films are candidate absorber layers for nanomaterials based, solution deposited up-conversion night vision devices operating in the short wave infrared (SWIR) range.[8]

References

2:45 PM BREAK

2:30 PM CP06.10.06
Characterization and Simulation of Elastocaloric Effects of Shape Memory Poly(Cyclooctene) and Its Composites Seok Bin Hong, Yongsan An and Woong-Ryool Yu; Seoul National University, Seoul, Korea (the Republic of).

The elastocaloric cooling effect of natural rubbers has been demonstrated for cold storage, however, its programming by cold-drawing is possible only at high strain rate. We found that shape memory cross-linked poly(cyclooctene) (PCO) exhibits enhanced elastocaloric cooling effect at relatively moderate strain rate due to its strain-induced crystallization behavior during cold-drawing [1]. The elastocaloric heating and cooling effects of PCO were predicted using Green-Lagrangian strains obtained from 3D finite element analysis (FEA) with a suitable constitutive model, which was already developed for shape memory polymers in our group [2], and thermodynamic quantities, showing good agreements between simulation and experiments. In addition, carbon fiber reinforced PCO composites were also studied to investigate the effect of carbon fibers on the elastocaloric effects of PCO. For the modeling of PCO composites, anisotropic hyperelasticity theorem was used for modeling the mechanical behavior of carbon fabrics. The interaction between fiber and SMP matrix depending on temperature change was considered through thermal residual stress [3]. Finally, an application of shape memory PCO and its composite to the elastocaloric refrigerator will be studied to demonstrate that implementation of the current method into 3D FEA can facilitate the design study of a portable cooling device made of shape memory polymers.


2:30 PM CP06.10.07
Tough and Water-Insensitive Self-Healing Elastomer for Soft Electronics Jiheong Kang and Zhenan Bao; Stanford University, Stanford, California, United States.

Electronic (e-) skin has recently been widely pursued as state-of-the-art wearable electronics due to its skin-mimetic mechanical and sensing properties. Similar to human skin, which is stretchable, tough, and even self-healable with sensing capabilities, efforts to render such e-skin devices robust and durable to withstand constant mechanical damage have led to various reports of self-healing elastomers. Even though elastomers utilized in e-skin devices are stretchable, but unfortunately, they easily break along locations where damages incurred due to their low fracture energies of ~100 J/m2 or lower. Furthermore, these damages are usually not self-healable[10]. Most self-healing materials are based on weak polymer systems with low fracture energies. Towards tough, self-healable and stretchable electronics for practical e-skin devices development, we report herein a polymer film cross-linked through multi-strength hydrogen bonding engineering. We further illustrate its application through the fabrication of highly stretchable and tough self-healing e-skin devices. We found the underlying principle for our tough and self-healable film is achieved through the spontaneous formation of a mixture of both strong and weak cross-linking hydrogen bonds. The strong cross-linking bonds confer robustness and elasticity, while the weak bonds are able to dissipate energy through efficient reversible bonds breakage and reformation. Furthermore, the polymer film is autonomously self-healable and highly moldable into desired complex 3D structures. Our film is easily hybridized with conductive fillers, in which we proceed to fabricate a new generation of e-skin: highly tough and stretchable self-healing system.

3:45 PM CP06.10.08
Yb:HfO:Eu3 Nanoparticles with High Concentration Quenching Towards Red Emitting Phosphor, X-Ray Scintillator and Luminescent Thin Film Yuanbing Mao1, Santosh Gupta1, Jose Zuniga2, Maya Abdou1, Santhosh Gupta1, Jose Zuniga2. 1The University of Texas at Rio Grande Valley, Edinburg, Texas, United States; 2Bhabha Atomic Research Centre, Trombay, India.

Desirable phosphors for light emitting diodes (LED) must have good light absorption property, high concentration quenching, high quantum efficiency, and narrow color emission, etc. In this work, we first show that undoped yttrium hafnate Y3Hf2O7 (YHO) nanoparticles (NPs) display dual blue and red bands after 330 nm light excitation. Based on Density functional theory (DFT) calculations, these two emission bands are correlated with the defect states arising in the band-gap region of YHO due to the presence of neutral and charged oxygen defects. Once doped with Eu3+ ions, the YHO NPs show bright red emission, long excited state lifetime and stable color coordinates upon near-UV and X-ray excitations. Concentration quenching is active when Eu3+ doping reaches 10mol% with a critical distance of ~4.4 Å. This phenomenon indicates a high Eu3+ solubility within the YHO host and the absence of Eu3+ clusters. The optical performance of the YHOE NPs has been further improved by lithium co-doping. Also, the YHOE NPs have been dispersed into PVA polymer to make nanocomposite films, which show strong red emission under excitations at 270 and 393 nm. Overall, high emission intensity and quantum efficiency
under UV and X-ray excitations make the YHOE NPs suitable as phosphors, scintillators and luminescent probes for LED and life science applications.

4:00 PM CP06.10.09
Localized Self-Growth of Reconfigurable Architectures Induced by a Femtosecond Laser on a Shape-Memory Polymer
Yachao Zhang1, Yanlei Hu1, Dong Wu1 and Chengwei Qiu2; 1Department of Precision Machinery and Precision Instrumentation, University of Science and Technology of China, Hefei, China; 2Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore.

Architectures of natural organisms especially plants largely determine their response to varying external conditions. Nature inspired shape transformation of artificial materials has motivated academic research for decades due to wide applications in smart textiles, actuators, soft robotics, and drug delivery. A “self-growth” method of controlling femtosecond laser scanning on the surface of a prestretched shape-memory polymer to realize microscale localized reconfigurable architectures transformation is introduced. It is discovered that microstructures can grow out of the original surface by intentional control of localized laser heating and ablation, and resultant structures can be further tuned by adopting an asymmetric laser scanning strategy. A distinguished paradigm of reconfigurable architectures is demonstrated by combining the flexible and programmable laser technique with a smart shape-memory polymer. Proof-of-concept experiments are performed respectively in information encryption/decryption, and microtarget capturing/release. The findings reveal new capacities of architectures with smart surfaces in various interdisciplinary fields including anti-counterfeiting, microstructure printing, and ultrasensitive detection.

4:15 PM CP06.10.10
Magneto-electric Coupling in 2D Multiferroics
Menghao Wu; Huazhong University of Science & Technology, Wuhan, China.

Multiferroics material with coupled magnetism and ferroelectricity, even though scarcely exist in nature, are highly desirable for efficient “electric writing + magnetic reading”. Currently, the polarization and magnetization of traditional multiferroics with strong magneto-electric coupling are all too weak for practical applications. Here we show first-principles evidences that strong magneto-electrics can be realized in a series of 2D multiferroics: in some intercalated bilayer systems, their “mobile” magnetism can be controlled by ferroelectric switching upon external electric field, exhibiting either “on” state with spin-selective and highly p-doped channels, or “off” state insulating for both spin and electron transport, which renders efficient electrical writing and magnetic reading; vertical polarization can be maintained against depolarizing field, rendering high-density data storage possible; moreover, all those functions can be directly integrated into a 2D wafer, like n/p channels by doping in a silicon wafer. In some 2D systems, the magnetization can be switched by 90 or even180 degree upon ferroelectric switching.

4:30 PM CP06.10.11
Roll-to-Roll Manufacturing of Flexible Sensors for Environmental and Food Pollutants
Susana Diaz-Amaya1, Li-Kai Lin1, Ana M. Ullou1, Mukerrem Cakmak1-2 and Lia Stanciu1-2; 1Purdue University, West Lafayette, Indiana, United States; 2Birck Nanotechnology center, Purdue University, West Lafayette, Indiana, United States.

The rapid expansion of sensors as a research field is continuously bringing to life novel materials, detection mechanisms and practical applications. During the last few decades a vast variety of sensors have been successfully developed at the laboratory scale demonstrating an enormous potential for solving global issues such as food and environmental pollution. Unfortunately, the fact that nearly 80% of the platforms developed at lab-scale never get to meet the market is not yet a common discussion within the field.

Challenges standing in the way of bringing sensors from the laboratory to the market include difficulties in reproducibility and repeatability. We used roll-to-roll processing to design field deployable flexible electrochemical sensors for the detection of environmental pollutants. Inkjet printed gold electrodes on flexible polyimide substrates were modified with a layer of specificity for organophosphorus pesticides and for mercury, respectively. We designed both platforms to transduce the target interaction signal by impedimetric (transfer charge resistance) response. For the pesticide sensor, a mesh of zirconium oxide fibers was deposited via roll-to-roll on the electrodes, leading to a detection of methyl parathion with a limit of detection (LOD) of 0.01 µM (r²= 0.952). The specificity was demonstrated vs nitrobenzene and 4-nitrophenol. Mercury ions were captured by a roll-to-roll deposited, thiol-functionalized aptameric sequence, highly specific for the target. The LOD for the Hg²⁺ was of 0.1 ppm (r²= 0.995) and the possibility to be re-used without significant variation was demonstrated. The platform specificity was assessed vs arsenic, cadmium and lead as potential interferent ions.

The results presented by this work reveal not only the high sensitivity and specificity of both capture strategies (zirconium oxide fibers and ss-DNA aptamer) but high stability, and repeatability in sensors response. We suggest it is now possible to incorporate roll-to-roll technology in sensor design, and take the high variety of already developed lab-scale devices to large-scale manufacturing.

4:45 PM CP06.10.12
Electrospinning and Plasma Treatment of Polyamides for Mosquito-Repellant Fabrics
Nicholas R. Etrick1,2, Chunhui Xiang1,2 and Margaret Frey2; 1University of Florida, Gainesville, Florida, United States; 2Human Ecology and Fiber Science, Cornell University, Ithaca, New York, United States; 3Apparel, Events, and Hospitality Management, Iowa State University of Science and Technology, Ames, Iowa, United States.

The need for light-weight, high-strength, and easily machineable insect-repellant fabrics is of critical importance to the cessation of viral diseases, such as Zika, Malaria, and Dengue Fever due to climate change.

In this study, the viability of electrospinning nanofiber Nylon-6 for use in protective garments will be investigated and compared to conventional polyamide fabrics, Nylon-6 Tricot and Nylon-6,6 Knit.

Throughout this investigation, the surface coating efficiency was evaluated to determine the best method of uptake for Permethrin, as well as characterization of fabrics utilizing DSC, TGA, FTIR, FESEM, XPS, GC-MS, Porometry, Tensile Testing, Rheometry, UV degradation, and washing fastness.

Acknowledgement: This work made use of the Cornell Center for Materials Research Facilities supported by the National Science Foundation under Award Number DMR-1719875.

SYMPOSIUM CP07

From Mechanical Metamaterials to Programmable Materials
April 25 - April 26, 2019

Symposium Organizers
Alexander Boeker, Universität Potsdam and Fraunhofer IAP
Christoph Eberl, Fraunhofer IWM
Silvia Titotto, Federal University of ABC
Xiaoyu Zheng, Virginia Tech

* Invited Paper
Bidirectional Self-Folding with Atomic Layer Deposition Bimorphs for Autonomous Micro-Origami

We present micron sized self-folding structures that consist of nanometer-thin, atomic layer deposited SiO$_2$-Si$_3$N$_4$ bilayers, built with conventional semiconductor fabrication methods. A bending response originating from strain differentials within these bilayer stacks is used for bidirectional fold actuation. This strain differential induced bending is controlled by ion exchange reactions in our nanoscale sheets, enabling us to produce radii of curvature at the order of microns within fractions of a second. By lithographically patterning these sheets and localizing the bending using flat photoresists panels, we create microscale origami devices that can sense chemical changes in their environment and respond by changing configurations according to prescribed mountain-valley fold patterns. Finally, we show that our fabrication approach offers a range of chemical, electrical and biological functions as well as a path to sequential folding through the programming of stacks.

Foldable and Responsive Soft Metamaterials

Reconfigurable soft metamaterials that can bend, fold, or transform the shape in response to external stimuli have attracted significant interests in design of actuators, sensors, and smart materials and devices. We fabricate a variety of periodically ordered, porous membranes with different size, shape and arrangement from responsive polymers, including poly(dimethylsiloxane) (PDMS), poly(2-hydroxyethyl methacrylate) (PHEMA) based hydrogels, and shape memory polymers (SMPs). By exploiting mechanical deformation in these material systems in respond to environmental cues, such as pH, heat, light, and mechanical stretching, we investigate pattern transformation, auxetic properties, and programmed deformation for pentiletal . We further design and synthesize nematic liquid crystal elastomers (LCEs), two-way SMPs, with large and anisotropic strains, and precisely align the monomers and oligomers within the patterned microchannels. In turn, we demonstrate pre-programmed folding of 2D sheets into 3D with various curvatures.

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Buckling Dominated Behavior of Elastic Hierarchical Truss Structures Matthew Begley, Geoffrey Wehmeier and Frank Zok; Materials Department and Department of Mechanical Engineering, University of California, Santa Barbara, Santa Barbara, California, United States.

The performance of porous materials with low relative density is limited by buckling of struts or cell walls, which reduces strength and energy storage during large deformations. Motivated by the expanding design space accessible via additive manufacturing, this paper examines the efficacy of combining multiple cell shapes and variable strut sizes to control buckling and improve compression response. A simple V-shaped cell between rigid platens is divided into sub-cells using smaller internal branches that run perpendicular to the loading direction (trapezoidal sub-cells) or at inclined angles (triangular sub-cells). Finite element simulations with linearly elastic beam elements that account for large rotations and self-contact are used to predict performance at fixed relative density. A broad parameter study will be illustrated showing the impact of sub-cell shape and strut size. Despite the simplicity of the structures, the simulations illustrate complex relationships between topology and post-buckling behavior that arise from highly non-linear kinematics. This complexity has important implications for the topology optimization of large deformation response of cellular solids. While performance can be highly sensitive to sub-cell geometry, the overall trends demonstrate that triangular sub-cells with small cross-sections (relative to the main V-struts) are effective in suppressing lower order buckling modes. Such structures exhibit improvements in peak stress and elastic energy storage of a factor of two or more, relative the undivided V-cell. The implications for designing low density materials are briefly discussed.

CP07.02.03
Auxetic Lattice Materials from Symmetry Breaking Pu Zhang and Quang K. Nguyen; SUNY Binghamton, Binghamton, New York, United States.

Auxetic lattice materials exhibit fascinating features like folding, expansion, and morphing due to their negative Poisson’s ratio. They play a significant role in the emerging family of mechanical metamaterials. It is well known that the negative Poisson’s ratio of auxetic lattice materials stems from specific deformation mechanisms, which have been the research focus in this area for decades. However, there is still a lack of systematic analysis of the deformation mechanisms of auxetic lattice materials. In this talk, we explore the relation between symmetry breaking and the evolution of Poisson’s ratio for lattice materials. The results offer in-depth understanding of auxetic materials from the symmetry principle and provide a promising way to discover new deformation mechanisms.

CP07.02.04
Shape Morphing Mechanical Metamaterials Michael D. Bartlett, Doh-Gyu Hwang, Sean Frey and A B M Tahidul Haque; Iowa State University, Ames, Iowa, United States.

Reconfigurable structures with tunable mechanical and functional response can enable dynamic functionality to improve performance and enhance versatility of materials and systems. One promising approach to create such structures is through the use of patterned folds or cuts in initially planar materials. Kirigami, the Japanese art of paper cutting, has demonstrated that the inclusion of cut patterns enables complex 3D structures from 2D sheets, elastic softening, and large deformations under external loading. Here we present reconfigurable and multistable mechanical metamaterials through the coupling of non-linear structural deformations with material non-linearities. First, we generate fabrication approaches to combine multiple material sets into a single material system through the combination of rapid prototyping through laser cutting and soft lithography. We then perform mechanical experiments to investigate the material and structural non-linearity upon deformation. Experimental results are supported by theoretical predications and simulations, which relate the material stiffness and deformation characteristics to the material composition and geometry. By tuning these parameters, we create 2D films which are capable of morphing into complex 3D shapes and then being electrically triggered to return to the initial 2D state. This work can enable substantial variations in stiffness and deformation of functional materials for applications in soft robotics, stretchable electronics, and human-machine interfaces.

CP07.02.05
Tailoring Materials Properties Outside Classical Bounds—Towards Mechanically Programmable Materials Peter Gumbsch, Christoph Eberl, Claudio Findeisen and Patrick Ziemke; 1Karlruhe Institute of Technology KIT, Karlsruhe, Germany; 2Fraunhofer IWM, Freiburg, Germany.

Ordinary materials neither exhibit multi-stability nor chiral mechanical response. This means that they cannot be stabilized in multiple conditions and that they do not convert stretch into twist. In contrast, metamaterials give access to such behavior. The design of such metamaterials to specific materials properties requires mechanistic materials modelling over multiple length scales to avoid tedious trial-and-error procedures and excessive experimentation.

Concerning chirality, Frenzel et al.[1] have created a chiral mechanical metamaterial and successfully mapped its behavior onto a micropolar continuum which predicts that the magnitude of the twist must decrease inversely proportionally to the ratio of the sample size to the size of one unit cell. To create chiral response for larger samples, the decay of the twist must be pushed to larger scales or eliminated. We first combine chiral unit cells with non-chiral coupling elements to form binary crystal structures exhibiting ultra-long decay-lengths compared to previous three-dimensional chiral mechanical metamaterials. We then proceed to generate structures that completely avoid this decay.

Multi-stability can be achieved with metamaterials that contain elastic buckling elements[2,3]. Gradients in the metamaterial in principle give access to a quasi-continuous regime of mechanical properties. Such graded metamaterials can be designed such that their effective materials properties can still be dramatically changed after manufacturing. I will take this as an example for an intrinsically programmable material. While the deliberate adjustment of locally different materials properties in a component may be regarded as the programming of a material to achieve component functionality, intrinsically programmable materials will allow realizing complex system functionalities including sensor and actor functions.


The Use of Negative Space Around Metamaterials to Improve the Performance of Energy Absorption Structures Dhruv Bhat, Christine Lee and Irving Ramirez Chavez; Arizona State University, Mesa, Arizona, United States.

One of the many potential applications of mechanical metamaterials is in the design of energy absorption structures used in functional components such as helmets and automotive crash structures. Traditionally, these structures have been manufactured using stochastic foams, but Additive Manufacturing (AM) process technologies have enabled the design of metamaterials with tailored and locally modified properties. The vast majority of literature on AM metamaterials for energy absporption have typically focused on the identification of a metamaterial unit cell shape that is optimal for energy absorption. In this work, we report on an alternative approach we have explored to incorporate “negative space” around metamaterials into the design of energy absorption structures.

The ideal energy absorption structure meets two objectives simultaneously - it provides high energy density, while also keeping the maximum transmitted stress to a low value. The former requirement ensures energy is absorbed with as little material as possible, which is important from a packing (in the case of a helmet) or light-weighting (in the case of an automotive crash structure). The objective of reducing the maximum transmitted stress is to keep the occupant safe and isolated from the effects of the stress.

In this work, we borrow the concept of “negative space” from the world of art, where it is typically used to describe the space around the subject. In art, negative space is often most evident when the space around a subject, and not the subject itself, forms an interesting or artistically relevant shape, and such space occasionally is used to artistic effect as the “real” subject of an image.

We used this concept to introduce negative space into a regular, periodic square honeycomb design with the intent of studying its effects on the mechanical properties of these honeycombs under compression. Our key finding in this work is that the introduction of negative space, particularly in the form of spiral patterns or as non-collinear spaces can
significantly increase the energy density for a given maximum transmitted stress. This data is collected using additively manufactured polymer honeycombs tested under compression. We leverage this empirical data to develop design principles that may be integrated into energy absorption structures more generally. While this work is limited to prismatic honeycombs, it is in principle, extendable to 3D metamaterials. On a more abstract level, we suggest that it is negative space, and not the metamaterial itself that may be functionally relevant for energy absorption and peak stress minimization, or at least play a complementary role along with the identification of an ideal metamaterial.

11:30 AM *CP07.02.07
Programmable Mechanical Metamaterials—Material, Machine and Everything in Between Matthew Berwind and Christoph Eberl; Fraunhofer-Institut fuer Werkstoffmechanik IWM, Freiburg, Germany.

The fundamental problem of how structure scales and size-dependently impacts materials has occupied humanity for centuries. Modern manufacturing techniques now allow us to investigate this basic question with incredible freedom, and rational design approaches to the structuring of materials can result in metamaterials with unique properties. A scale-bridging understanding of how structure defines such a metamaterial independent of its base composition is necessary for this rational design process to be successful. Herein we examine metamaterials with a view spanning their internal ‘mechanisms’, the unit cell, its connectors, and finally the resultant matrix with its hierarchically subordinate components. Some recent efforts in the development of programmable mechanical metamaterials, or designed materials that respond to external stimuli in a discrete and ideally reversible fashion, will be presented that rely on a clear understanding of rational hierarchical design approaches.

SESSION CP07.03: Programming Mechanical Properties
Session Chairs: Jens Bauer and Xiaoyu Zheng
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 106 A

1:30 PM *CP07.03.01
Programmable Properties of Two-Photon-Polymerized Materials and Metamaterials Jens Bauer, Cameron Crook, Anna Guell and Lorenzo Valdevit; University of California, Irvine, Irvine, California, United States.

From the current perspective, there is little room for further expansion of the accessible material property space by classical material fabrication methods. Single one- and two-dimensional nanoscale objects, such as nanowires and thin films, are known to hold exceptional physical properties. Yet, their properties are intrinsically coupled to their small size and their solitary nature, and therefore can hardly be accessed in actual materials of practical volume. If nanowires and thin films are simply scaled up properties, which relate to surface to volume effects, get lost, when clustered in a composite interfaces dominate the overall performance. Nanomachined metamaterials are regular three-dimensional networks constructed from nanowires or thin films and have the potential to overcome such limitations. Two-photon polymerization (TPP) is the most versatile technology for fabricating nanomachined metamaterials and rapidly progresses towards higher throughput, resolution and a broader spectrum of printable materials. However, TPP fabrication is still largely empirical without systematic data on material properties and limited knowledge on their dependency on the process parameters. In this work, we systematically characterized the mechanical properties of two-photon polymerized resins as well as corresponding pyrolytic ceramics, from nanowires to bulk specimens. We show that the properties of the material systems can be tailored from rubbery soft to hard and strong, and explain the observed behavior by a photonics-based model allowing to predict the mechanical properties of two-photon polymerized materials depending on applied process parameters. In a second step we incorporated specifically designed material properties in different nanomachined metamaterials. We discuss the interplay of material design approaches, size-effects and different topological designs and show unique effective characteristics such as mechanical performance at the theoretical limit of both the architecture and the constituent material.

2:00 PM CP07.03.02
Meta-Crystals—A Fusion of Physical Metallurgy and Architected Materials Son Pham; Materials, Imperial College London, London, United Kingdom.

I will present a transformative idea of designing meso-structures (termed as meta-grains, meta-precipitates and meta-phases) that imitate key microstructures (namely crystal grains, precipitates and phases) in crystalline metals to generate a new type of meta-materials: meta-crystals. This mimicry enabled by additive manufacturing opens a unique opportunity to employ the key hardening mechanisms found in metallurgy to the design of architected materials. This study demonstrates that such meso-structures play the same roles on governing the properties of meta-crystals as do intrinsic microstructures in metallic alloys, opening up a new space of designing lightweight and damage-tolerant materials with desired properties.

2:15 PM CP07.03.03
Mechanical Meta-Materials Inspired by Crystal Microstructure—Size Effect and Anisotropy Chen Liu and Minh-Son Pham; Department of Materials, Imperial College London, London, United Kingdom.

Mechanical meta-materials that mimic the crystal lattices are lightweight and hold great potential for a wide range of applications, such as aerospace, automobiles and medical devices. However, previously reported lattice meta-materials consisted of lattices that are singly oriented. Such lattice meta-materials are analogous to single crystals, and normally exhibit unstable deformation behaviour due to the occurrence of single shear bands throughout the whole lattice, resulting in substantial reduction in energy absorption. In this study, we present a novel approach to mimic the polygranular structure in metallic alloys and bring the grain-size hardening effect in polycrystals to develop polycrystal-like meta-materials. We found that the boundaries separating meta-grains play an influential role in the propagation of shear bands in the same way as the grain boundaries do in slip activities in metals. Most interestingly, the strength of polycrystal-like meta-material is found to increase with decreasing the size of meta-grains, similar to the Hall-Petch relationship. Moreover, this talk will demonstrate that we can engineer the crystal-like lattice structures to tune the meta-material properties in the same way as the microstructure engineering in metallurgy. The tailoring of anisotropy of meta-materials will be presented as an example.

2:30 PM BREAK

SESSION CP07.04: Manufacturing Architectured Materials
Session Chairs: Jens Bauer and Xiaoyu Zheng
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 106 A

3:00 PM *CP07.04.01
Three-Dimensional Photonic Manufacturing—From Catalytic Waste Gas Converters to Microvascular Tissue Scaffolding Nicholas Fang; Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Three-dimensional lightweight material building blocks, through the combination of molecular design of material behavior and microscale geometric patterning, show promise to revolutionize the ability to dissipate energy and manipulate wave propagation. Such materials are desirable for a broad array of applications such as structural components, catalysts supports and energy efficient materials.

In this invited talk, I will present our development of three dimensional micro/nanofabrication technique, projection microstereolithography (PuSL), to enable design and
exploration of digitally coded multifunctional and multimaterial lightweight metastructures at unprecedented dimensions. The ultra-high resolution and multi-material capabilities of the 3D printing system and the modeling tools developed can be used to design and fabricate architectured materials for combined functions, including energy absorption, actuation/morphing, and reactors with fast thermal response and efficient convection of working fluids. I will also discuss the development of engineered, three-dimensional arrays of copolymer fibers that serve as mimetics of neuronal axons, using a combination of materials engineering and high resolution 3D microfabrication, which enable study of OPC engagement and subsequent myelination in vitro.

3:30 PM CP07.04.02
Site Selective Laser Shaping of Architected Mechanical Metamaterials
Letian Wang, Zacharias Vangelatos and Costas Grigoropoulos; University of California, Berkeley, California, United States.

Multiphoton lithography is the widely used 3D micro-printing method that enable fabrication of architectured microstructures in length scales of 1 um. However, the further reduction of the feature size and the printing of curved surfaces still remain challenging. Here we report that the focused laser beam can induce localized pyrolysis on polymer-ceramic hybrid architectured materials. The minimum feature size is reduced from 400nm to 250nm, yielding a volume reduction factor of 2.56. With nanodiamond experiments, we confirmed that a top-down z-dependent deformation on the architectured metamaterial introduces an 100% enhancement in mechanical strength. Additionally, in-plane 2D xy-dependent deformation generates controllable curved surfaces from straight lattice struts. Hence, the laser induced site-selective deformation offers on-demand modification of the physical geometry and mechanical properties for architectured metamaterials.

3:45 PM CP07.04.03
3D Printing of Zinc Oxide via a Novel Photopolymer System
Darel Vee, Max L. Lifson and Julie Greer; Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States.

In recent years, 3D printing of ceramics has become a significant area of interest as it has the potential to remove the geometrical limitations associated with the current state of the art of ceramic processing. In particular, 3D printing processes involving photolithography have emerged as some of the most promising ones due to the high resolution and small feature sizes achievable. These photolithography systems typically consist of photosensitive slurries, where fine powders of the desired ceramic of choice are dispersed in a photosensitive organic binder. By selectively exposing certain parts of the slurry to radiation of the appropriate wavelength, the binder can be cured into a desired shape, trapping the ceramic powder within as well. A subsequent high temperature treatment then burns off the organic binder and sinters together the remaining ceramic powders into a dense ceramic part. The advantages of these systems are that it’s simple and versatile – as long as the desired ceramic can be obtained in powder form and can be dispersed in a photosensitive binder, the slurry can be obtained and the part printed. However, for a part to survive the high temperature process, the slurry has to have a high loading of ceramic particles, somewhere between the ranges of 45-70 volume percent, which results in a host of other issues. At such high loadings, the viscosity of the slurry increases significantly, making it difficult to print. Homogeneous dispersion of the ceramic powder also becomes challenging at such high viscosities. Furthermore, the solid ceramic particles increase the refractive index of the resin and scatter the incident light, reducing both the cure depth and the dimensional accuracy of the print.

In this presentation, a new photopolymer system that circumvents the problems of powder loading is demonstrated. The photopolymer system is simple to make and can be easily modified to fabricate various multifunctional metal oxides. As an example of this technique, we demonstrate the printing of zinc oxide (ZnO) architectured structures. ZnO is traditionally deposited as films and can only be made 3D via a multistep process that involves depositing a thick layer of ZnO and then using an ion-mill to cut out the structure desired. Here, we show a two-step process to fabricate monolithic 3D ZnO structures out of any arbitrary design. Characterization of these structures using X-ray diffraction, energy-dispersive spectroscopy and transmission electron microscopy indicate that the structures are indeed zinc oxide. Compression of these materials also results in a voltage response, showing the piezoelectric behavior of these structures. The ability to fabricate these multifunctional 3D materials could open up the field of smart devices and change how we design them.

4:00 PM CP07.04.04
Atomic Layer Deposition for Membranes, Metamaterials and Machines
Tanner Pearson1, Kyle J. Dorsey1, Edward Esposito2, Baris Bircan1, Yimo Han3, Sierra Russell2, David Muller1, Itai Cohen2 and Paul L. McEuen1; 1School of Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; 2Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York, United States; 3Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York, United States; 4State University of New York Polytechnic Institute, Albany, New York, United States.

Ultra-thin films of inorganic materials are well-suited for fabrication of micron-scale actuators because they can sustain small radii of curvature, have large force outputs, are compatible with semiconductor processing, and are chemically robust. We leverage atomic layer deposition (ALD) on sacrificial substrates to produce micron-scale free-standing mechanical devices with sub-10 nm film thicknesses. We fabricate cantilever springs from ALD films and characterize the material’s mechanical properties. We find that ALD films are remarkably elastic and exhibit a bending stiffness on the order of femtometers. These measurements enable fabrication of cantilever springs with tailorable ultra-low spring constants suitable for micron-scale machinery. The mechanical properties of ALD are further characterized by lithographic patterning of both the ALD film and its substrate in the design of mechanical metamaterials. Substrate corrugations transferred into the ALD film enhance its bending stiffness and allow programmable bending anisotropy, while lattices imposed into the film decrease its effective Young’s modulus for stretchable and auxetic materials. We integrate these results and device concepts to produce magnetically actuated three-dimensional structures with applications in micromachining. Our results establish thin ALD films as a scalable basis for micron-scale actuators and shape-programmable microrobots.

4:15 PM CP07.04.05
Controlling Magnetic Properties in Fused Deposition Modeling Parts via Shape, Infill Orientation and Infill Percentage
Thomas M. Calascione, Mike V. Patton, Andrew H. Morgenstem, Nathan Fischer and Brittany Nelson-Cheeseman; University of St. Thomas, Saint Paul, Minnesota, United States.

Fused deposition modeling (FDM) is an additive manufacturing (aka 3D printing) process that extrudes viscous material in 1-dimensional lines to create 2-dimensional layers that build up to a 3-dimensional part. The creation of magnetic composite parts is just beginning to be explored with FDM. Previous work has found the out of plane direction (perpendicular to the print plane) to be a magnetically hard axis. This motivated further investigation into the influence of specific print parameters on the magnetic properties of parts, as this has not yet been fully characterized. The ability to mechanistically manipulate materials via magnetic fields (such as magnetic shape memory alloys, magnetostrictive materials, and magnetothermoelectric materials) means that tailoring the magnetic properties of such materials is intimately tied to tailoring their performance over time (i.e. 4D-structures). Here, we explore this topic with a composite magnetic filament consisting of PLA and polyacrylonitrile to print 4D-printed structures where the magnetic response is “programmable”. This filament was used in an FDM process to print magnetic samples of varying length, width, infill percentage, and infill print orientation. The length and width variables resulted in parts of two different macroscopic dimensions: 5mm by 10mm (anisotropic) and 10mm by 10mm (isotropic), both with a height of 2mm. The infill percentages printed were 60%, 70%, 80%, 90%, and 100%. The infill print orientation refers to the direction the printer extruded the 1D filament in order to create the part shape, either along or against the shape anisotropy. From these variables, and since the square samples required only one set of prints to get both print orientations due to symmetry, there were 12 unique parts. Three of each were printed, resulting in a total of 36 parts that were tested. A vibrating sample magnetometer (VSM) was used to determine the effect of these different print structures on the magnetic response to a maximum applied magnetic field of 1.4 T. Hysteresis loops for each sample were measured with the magnetic field applied along the longitudinal and transverse directions of the part, resulting in 72 total tests. This data was used to compare the magnetic susceptibilities between the different print structures. After preliminary testing, all parts were tested again for consistency of procedure and data acquisition. The results show that infill orientation has a prominent effect on the magnetic properties. At lower infill percentages, magnetic susceptibility is greater parallel to the infill orientation. However, as infill percentage increases, this effect diminishes, and the effect of the macroscopic shape then has an equal effect on magnetic susceptibility as the infill orientation. The infill orientation anisotropy effects are reduced at higher infill percentages due to the minimization of air gaps that magnetic flux lines must traverse going through the sample. Determining how shape, infill orientation, and infill percentage affect the magnetic properties of printed parts will help in understanding how an FDM process can be developed to “program” these properties in order to manipulate the mechanical performance of 4D-materials, incentivizing FDM as a method for manufacturing magnetic components.
Controllable Elastomer Shape Modulation with Solvent Droplet Sequence Akshay Phadnis and Konrad Rykaczewski; Arizona State University, Tempe, Arizona, United States.

Stimuli sensitive polymers that swell in response to interaction with various solvents offer possibilities to achieve controllable shape transformations. Temporal interaction of these materials with solvent, when controlled locally, can be translated into programmable shape modulation. These geometrical transformations occur over a time scale that depends upon the solvent and the material properties, as well as the size/shape of the material and thus can be easily controlled. Here, we use coupled experimental and theoretical methods to quantify geometry dependent shape transformations of rubbery materials that are locally subjected to a train of solvent droplets. Based on relative comparison between diffusion time scale and droplet pulse period, we identify regimes where such shape transformations can be achieved and controlled. This regime is achieved when the two timescales are comparable whereas equilibrium swelling occurs at two extremes of this scaling. To demonstrate the various regimes, we study swelling of six cylindrical geometries of PDMS with varying aspect ratio subjected to pulsating drops of n-hexane. As a result, a localized swelling feature incremental in time and space domain is observed. Furthermore, we show that the characteristic of this swelling feature depends strongly on the sample aspect ratio relative to the droplet size. We demonstrate this using two cases of cylindrical geometries and a custom finite element model. We use this validated model to predict the geometries of rest of the cases and show dependence of characteristic swelling feature on sample aspect ratio. These deformations are magnified during the droplet-train impact but dissipate during post-train polymer equilibration. Our results also show that while swelling shape is a function of lateral dimensions of the sample, with the extent of swelling increases with the elastomer sample thickness.

References

Block Copolymer-Templated Nanoceramics with Ductile-Like Compression Behavior Lisa Rueschhoff, Robert Wheeler, Hilmar Koerner, Matthew Dalton, Michael Cinibulk and Matthew B. Dickerson; Air Force Research Laboratory, Wpafb, Ohio, United States.

Nanoscale structured ceramics and composite compositions can exhibit extraordinary mechanical properties, including elastic deformation and high toughness. In this presentation, we will discuss a highly-scalable system that exploits polymeric self-assembly and ceramic precursors to produce inorganics with mechanical metamaterial properties. Here, block copolymers (BCPs) serve as templates for the structuring of preceramic polymers (PCPs). The heat treatment of these materials allows for the concurrent curing of the PCPs, removal of the BCP template, and finally conversion of the PCP to ceramic. Using this method we have created novel SiC-based ceramic structures with nanoscale features and porosity. Insight into the relationship between polymer chemistry and structure in thin films of this BCP/PCP system, as well as in-situ mechanical characterization of porous ceramic micropillars, will be presented.

The Implementation of Periodic Topologies and Acoustic Metamaterials to the Design of Infrastructure Systems Didem Ozevin; University of Illinois at Chicago, Chicago, Illinois, United States.

It is inevitable that structures including bridges, pipelines, and aircraft eventually develop cracks. Unfortunately, current design practice does not include the means of structural damage detection into the design process. In this paper, periodic superstructure and substructure are induced at pre-design and post-design processes in order to control dynamic response of structure and generate local resonators and redirect/control elastic waves, respectively. For the pre-design process, various truss topologies are configured with a periodic pattern for monitoring their variations with localized damage using the impulse response method independent from boundary conditions. For the post-design process, the presence of damage is monitored by Structural Health Monitoring (SHM) methods. Among many SHM methods, Acoustic Emission (AE) method has advantages of being non-intrusive, direct assessment of damage and localization. The major disadvantage of AE method is the sensitivity to background noise. Two-dimensional phononic crystal (PC) is designed to block unwanted background noise such that single AE sensor becomes sufficient to monitor the active flaws as fatigue crack and corrosion. The other application of applying acoustic metamaterials to structural systems is the isolation of building superstructure from any dynamic loading through periodic substructure design with the band gap range of dynamic signal. The integration of periodic systems and acoustic metamaterials brings unique characteristics to the long term durability and resilience of infrastructure systems.
of local defects in architectured materials play an important role in the formation of domains separated by distorted domain boundaries and analyze such phenomenon with a statistical mechanics model analogous to the Ising model. Our study provides a pathway for predicting dynamic architectured material responses according to defect density and distribution, which has not been discussed in previous works. With this understanding, we designed and implanted artificial defects in Si microlattices to deterministically control buckling directions to produce single-domain sinusoidal lattices and to program domain boundaries that form a particular pattern. This new class of architectured materials provides insights for next-generation battery electrodes with novel stress-relief mechanisms and dynamic mechanical metamaterials with tunable phononic bandgaps.

10:15 AM CP07.06.02
Strain Rate Dependence of Additively Manufactured Polymer, Composite and Metallic Honeycomb Structures Dhairaj Patil1, Mandar Shinde1, Thao Le1, Quoc Lam1, Derek Goss1, Alex Grisin1 and Dhruv Bhat1, 1Arizona State University, Mesa, Arizona, United States, 1Phoenix Analysis & Design Technologies, Inc., Tempe, Arizona, United States.

Metamaterials are experiencing a resurgence in engineering application on account of Additive Manufacturing (AM) since it is now increasingly possible to manufacture complex geometries that include these structures. Manufacturing parts with mechanical metamaterials have several advantages: lower material and energy utilization in the manufacturing process as well as lifetime savings due to the product’s higher performance, especially in weight sensitive domains such as transportation (ground, air, or space).

Despite the significant potential of combining metamaterials with AM, there has been limited implementation in end-use functional parts. A key challenge to realizing this goal stems from our inability to model and predict metamaterial behavior reliably. This is on account of several relatively well-understood reasons including sensitivity to geometric tolerances and microstructure variation at small scales. In this work however, we focus on an aspect of characterizing and modeling metamaterials that has not received enough attention in the additive manufacturing literature, and that is the fact that these materials are highly sensitive to strain rate. This is true at “quasi-static” strain rates, and not just at the higher strain rates associated with impact. We examine the underlying reasons for this, showing how local strain rates can significantly exceed those applied globally.

To simplify our ability to characterize and model observed behavior, we limit our study of strain rate dependence to hexagonal honeycombs across four different additive manufacturing processes: one polymer (Fused Deposition Modeling with ABS), one composite (Nylon and Continuous Carbon Fiber Extrusion) and two metallic (Laser Powder Bed Fusion of Inconel 718 and Electron Beam Melting of Ti6AI6V). We compare strain rate sensitivities of the effective elastic modulus and peak load for all four processes. We also report on strain rate sensitivities for the polymer honeycombs for five different shapes: hexagonal, square, triangular, Voronoi and for a graded structure that induced buckling failure. In all cases, significant strain rate sensitivities were observed from applied nominal strain rates ranging from 1 to 10^5 s^-1. Finally, we use beam theory and Finite Element Analysis to model this strain rate dependence for the polymeric material and show that the inclusion of strain rate dependence is essential for the accurate plastic-plastic modeling of honeycomb deformation. This study has implications for the characterization and modeling of all mechanical metamaterials and suggests that accurate representation of these structures must include strain rate effects.

10:30 AM CP07.06.03
High Strain Hardening, Lightweight, Three-Dimensional Mechanical Metamaterials with Microlattices Inspired by Crystal Twinning Zacharias Vangelatos, Kyriakos Komvopoulos, Costas Grigoropoulos and Letian Wang1; Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States.

Mechanical metamaterials exhibit enhanced properties derived from their architecture. Advances in 3D printing techniques have enabled the fabrication of complicated designs even at the microscale, contributing to the progress of state of the art ultra light materials with superior mechanical features. Nevertheless, comprehending the mechanism of strain hardening that is an inherent characteristic to the structure and arrangement of the unit cells is rather limited and fairly empirical. In this study, we present a novel design of mechanical metamaterial structures influenced by the first stellation of rhombic dodecahedron, and juxtapose its mechanical behavior with one of the most meticulously studied metamaterial designs, the octet truss and its counterpart bulk material. The uniqueness of the present design is the adaptation of crystal twinning in a two-level design process of the unit cells, that is, the architecture of unit cells and their connection to adjacent unit cells. Our findings validate that this design strategy is highly efficient in enhancing the metamaterial’s strength and energy absorption potential, while simultaneously diminishing the volume occupied by the structure considerably. By performing simulations and nanoindentation tests for these metamaterial structures fabricated by two-photon lithography, we have proven that this new type of metamaterials surpasses both the bulk material and the octet truss structure, as indicated by the remarkably higher strain hardening and energy dissipation characteristics obtained for the same deformation, despite the significantly smaller volume of the first stellation structure. Our study introduces a novel design technique for controlled strength and strain hardening in mechanical metamaterials by the strategic placement of simple platonic solids to form more complex structures with deformation modes resembling those of microlattices that exhibit crystal twinning.

10:45 AM CP07.06.04
Acoustic Metasurface Yun Jing; Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Wave manipulation using artificial materials is a central topic in materials physics. Recent years have witnessed the emergence of a family of thin, 2D artificial materials, namely, metasurfaces. The concept of metasurfaces was introduced to the materials and physics communities for optical waves in 2011 with the generalized Snell's law, which opened up a new degree of freedom for optical wave manipulation. Inspired by this pioneering work, and because acoustic waves also follow the Snell's law, a flurry of activity has revealed acoustic metasurfaces for controlling sound and new applications in acoustics. However, mapping the success of electromagnetic metasurfaces to the acoustic domain is challenging, primarily owing to the intrinsic differences between electromagnetic and acoustic waves. In this talk, I will delineate the underlying fundamental physics of metasurfaces, describe their different concepts, the design strategy, and discuss their functionalities for controllable reflection, transmission, and extraordinary absorption. In particular, I will discuss our recent works on acoustic metasurface-based ultrathin sound diffusers and gradient-index metasurface-induced asymmetrical sound transmission.

11:15 AM CP07.06.05
Engineering the Shapes of Organic crystals to Generate Different Photomechanical Responses Fai Tong1, Rabih O. Al-Kaysi1 and Chris Bardeen1; 1Department of Chemistry, University of California, Riverside, Riverside, California, United States; 1College of Science and Health Professions, King Saud bin Abdulaziz University for Health Sciences, and King Abdullah International Medical Research Center, Ministry of National Guard Health Affairs, Rayadh, Saudi Arabia.

Solid-state photochemical reactions in molecular crystals can generate large-scale motions and shape changes. These photomechanical crystals have potential applications as light-controlled actuators and smart switches. Micro- and nanocrystals can exhibit motions like bending, twisting, curling, and jumping under light illumination. However, controlling the size and shape of molecular crystals remains a challenge because the weak van der Waals intermolecular forces between organic molecules undermine their ability to lock in a specific shape during crystallization. Besides the overall crystal shape, the orientation of the molecules within that shape should also play an important role in determining the photomechanical response. In general, the arrangement of molecules in a crystal are determined during the early stages of crystallization process. Recently, our group developed a surfactant-assisted seeded growth method to prepare single crystal platelets composed of 9-methylanilinacene (9MA) with two different internal molecular orientations in aqueous solution. The more stable form exhibits a photoinduced twisting motion and elongated hexagonal platelets undergo a photoinduced rolling-up and unrolling which can be used to wrap and translate magnetic nanoparticles with external magnetic field applied. What is more, we have extended our seed-growth technique to other anthracene derivatives. We had successfully grown uniform block-like microcrystals composed of cis-dimethyl-2,3-(anthracen-9-y)ylidylene)malonate (cis-DMAAM) in aqueous surfactant solutions. A brief pulse of light (< 405 nm) causes these crystals to undergo delamination (peeling). This peeling process can be repeated multiple times on the same microblock, uniformly peeling off layer after layer with a train of light pulses. Our results demonstrated how tuning crystal morphology (size and shape) can lead to novel modes of mechanical behavior. This novel crystal growth method generates new crystal shapes that illustrate the versatility of photomechanical molecular crystal materials.

11:30 AM CP07.06.06
Towards Programmable Optical Metasurfaces Isabelle Staude and Jürgen Sautter; Friedrich Schiller University Jena, Jena, Germany.

Optical metasurfaces composed of designed Mie-Resonant semiconductor nanoparticles arranged in a planar fashion offer unique opportunities for controlling the properties of light fields [1]. Such metasurfaces can impose a spatially variant phase shift onto an incident light field, thereby providing control over its wave front with high transmittance efficiency. They can also e.g. act as polarizing optical elements, exhibit tailored nonlinear optical properties, or manipulate spontaneous emission processes of nanoscale emitters integrated in the metasurface architecture. However, the optical response of most semiconductor metasurfaces realized so far was permanently encoded into the metasurface structure during...
fabrication. Recently, a growing amount of research is concentrating on obtaining dynamic control of their optical response, with the aim of creating metasurfaces with functionalities that can be programmed on demand. This talk will provide an overview of our recent advances in actively tunable Mie-resonant semiconductor metasurfaces. In particular, by integrating silicon metasurfaces into a liquid-crystal (LC) cell, we can tune their linear-optical transmittance and reflectance spectra by application of a voltage [2]. Importantly, this tuning approach is highly compatible with established LC industrial technologies. We, for the first time in our knowledge, utilize a LC photodalignment material [3] during the assembly of the LC metasurfaces, leading to a drastic improvement of the tuning performance and reproducibility. Based on this method, we demonstrate two electrically tunable LC-infiltrated dielectric metasurfaces working at near-infrared and visible wavelengths respectively. We show that these metasurfaces can be tuned into and out of the so-called Huygens’ regime of spectrally overlapping electric and magnetic dipolar resonances, which is characterized by near-unity resonant transmission, by application of an external voltage. In particular, we propose a novel route toward phase-only tuning by applying simultaneous electrical and thermal stimuli to the LC-infiltrated dielectric Huygens’ metasurfaces. However, while the integration of silicon metasurfaces into nematic LC cell represents an efficient and versatile tuning approach showing large resonance shifts and strong contrast tuning, the switching times that can be achieved based on this approach are limited. Thus, as an alternative tuning mechanism allowing for ultrafast operation, we consider the transient changes of the optical properties of semiconductor materials when optically pumped by femtosecond laser pulses. These changes can lead to pronounced changes of the resonance condition for semiconductor metasurfaces at an ultrafast time scale. This talk will review our recent progress in ultrafast switching and tuning of semiconductor metasurfaces based on different material platforms and different physical mechanisms occurring at an ultrafast time scale [4,5]. Furthermore, strategies to translate ultrafast tuning of metasurface resonances to ultrafast control of more complex metasurface functionalities such as wavefront shaping will be discussed.


SYMPOSIUM CP08

Additive Manufacturing of Metals
April 23 - April 24, 2019

Symposium Organizers
Moataz Atallah, University of Birmingham
Dawnielle Farrar-Gaines, Johns Hopkins University
Krystafeux Williams, United States Naval Research Laboratory
Jennifer Wolk, Office of Naval Research

* Invited Paper

SESSION CP08.01: Characterization—Microstructure Analysis and Mechanical Behavior I
Session Chairs: Dawnielle Farrar-Gaines and Jennifer Wolk
Tuesday Morning, April 23, 2019
PCC West, 100 Level, Room 106 A

10:30 AM CP08.01.01
Effect of Nucleating Particles on the Microstructure of 7075 Al Alloy Manufactured by Selective Laser Melting

Additive manufacturing has the potential to disrupt traditional fabrication methods for high add value applications because the flexibility of design, fast production speed for complex parts, and shorter lead times. However, there is currently a reduced range of metallic alloys that can be industrially processed using this technique. This is particularly problematic in the case of high strength Al alloys processed by additive manufacturing which present high porosity and an undesired microstructure formed by large columnar grains surrounded by longitudinal cracks (hot-cracking). It has been recently shown [1] that these problems can be overcome through the addition of ZrH2nanoparticles to the Al powders. In particular, hot cracking was significantly reduced and the microstructure was refined due to the stimulation of grain nucleation by the nanoparticles. In this investigation, a systematic study was carried out to analyze the effect of processing parameters (laser power and speed hatch distance) on the microstructure of 7075 Al alloy. Commercial powders of the 7075 Al alloy were mixed with zirconium dihydride particles by planetary milling without any grinding medium. Samples were additive manufactured by selective laser melting with and without zirconium hydride particles, using a wide range of process parameters. The microstructure of the processed samples was characterized by electron backscattered diffraction (EBSD), electron microscopy and transmission electron microscopy (TEM) in order to evaluate the influence of the addition of refining particles along the building direction.

The addition of ZrH2 led to an equiaxed grain structure (which was attributed to enhanced nucleation promoted by the Al-Zr precipitates) and to the elimination of hot cracking. A hardness increase of 30HV was observed in the Zr containing samples probably due to the hardening effect of an enhanced precipitate volume fraction. The effect of processing parameters on the microstructural features and on the hardness was analyzed.


10:45 AM CP08.01.02
Microstructure and Mechanical Properties of 316L Stainless Steel Fabricated Using Selective Laser Melting
Naveed Iqbal, Enrique Jimenez-Melero, Utkarsha Ankalkhope and Jonathan Lawrence; University of Coventry, Coventry, United Kingdom; University of Manchester, Manchester, United Kingdom; Manufacturing Technology Centre, Coventry, United Kingdom.

The microstructure variation and heterogeneity in mechanical properties of 316L stainless steel fabricated using selective laser melting (SLM) have been investigated. The crack free, dense samples were made using SS316L alloy powder and melt pool morphology was analysed using optical and scanning electron microscopy. Extremely fast cooling rates during laser melting/solidification process, accompanied by slow diffusion of alloying elements, produced distinct microstructure with colonies of fine-grain size as well as elongated grains grown along the direction of thermocapillary convection in the melt pool. Precipitates were mostly observed at the grain boundaries while some times also appeared inside grains. The micro hardness measurements along the build direction revealed slight but gradual increase in hardness along the sample height. The tensile tests of as build samples showed that the mechanical properties of samples produced using SLM were observed to be quite heterogeneous. The ultimate tensile strength (UTS) varied from 460MPa to 510MPa along with elongation variation from 3% to 15%. The corrosion behaviour of SLM samples were also investigated by exposing the tensile samples to 5% NaCl.

Corrosion properties and mechanisms of additive manufacturing (AM) alloys have shown to differ from traditional wrought and cast manufacturing methods relative to polarization and corrosion/fatigue. While a significant portion of published data indicates favorable yield, ultimate, and elongation mechanical properties, the practical discussion of structural and environmentally conditioned loading is a relatively unaddressed consideration in the design of AM metals. The discussion of this presentation addresses the standard polarization behavior of AM metal materials relative to as-built, heat treated, and variable controlled powder bed fusion and directed energy deposited metallic alloys, as well as initial reaction/formation of powder bed fusing processes and how they relate to various corrosion properties. Standard polarization testing of AM materials often indicates that AM metals compare favorably to wrought or cast pitting potentials in the laboratory setting, however crevice corrosion is accelerated even in the most controlled test environments. The US Naval Research Laboratory has studied the effects of AM materials in marine environments relative to their pitting, crevice and fatiguer corrosion/fatigue properties in order to more appropriately assess AM metals’ application to marine and naval designs. To that end, this presentation discusses the relationship of various AM processing parameters, powder feedstock, and post build processing relative to corrosion performance in seawater environments common to naval applications.

Materials tested to date include 316L stainless steel, titanium 6-aluminum, 4-vanadium and Inconel 625 alloys built using additive manufacturing produced by the laser powder-bed-fusion process (L-PBF) and directed energy deposit (DED) processes with the principal test in axial an transverse orientations. High cycle fatigue and corrosion fatigue properties of these metals were measured using crack opening compact tension fatigue and environmental fatigue ASTM standard practices. The fatigue and corrosion fatigue limits of these materials in high cycle fatigue were determined. The fatigue crack growth rate behavior in air was characterized and compared with information available in the literature. Furthermore, standard fatigue and fracture test protocol according to the most modern fatigue crack growth rate standardized procedures was completed with mixed results as a function of AM specific mechanisms affecting data production.

Laser Metal Additive Manufacturing onto Silicon Arad Azizi, Matthias A. Daemener and Scott N. Schifffres; Mechanical Engineering, Binghamton University, Binghamton, New York, United States.

We demonstrate how Sn3Ag4Ti alloy can robustly bond to silicon via selective laser melting (SLM). By employing this technology, thermal management devices (e.g., vapor chamber evaporators, heat pipes, micro-channels) can be directly printed onto the electronic package without using thermal interface materials. Reduction of the chip operating temperature up to 10 °C, consumed power and electronic-waste are some of the advantages of this technology which lies through the elimination of thermal interface materials in the electronic package. Bonding of common metal alloys used in additive manufacturing and silicon is relatively weak and generally possesses high contact angles (poor wetting and interfacial strength). However, reactivity and wettability of the silicon substrate increases drastically by using proper interlayer material. Furthermore, conventional dissimilar material bonding can take tens of minutes to form a strong bond, this study demonstrates how this kinetic limitation can be overcome to form a bond in microseconds via intense laser heating. Rapid bonding of Sn3Ag4Ti to silicon occurs through formation of a thin (~μm) titanium-silicide interfacial layer that makes the silicon wettable to the Sn3Ag4Ti. This rapid bonding occurs due to formation of strong intermetallic phases at low temperature, and by exposing of the sample by laser multiple times which provides sufficient diffusion time. The printed parts are mechanically robust with no visible failures after over a week of continuous thermal cycling (~40 °C and 130 °C).

Spotlight Talk—Optimization of Process Parameters for Additive Manufacturing Using Recycled Metal Powder Susana J. Castillo1, Anna K. Hayes1, Krishna Muralidharan1; Gregory Colvin1, B.G. Potter and Melissa Bushi1; University of Arizona, Tucson, Arizona, United States; ‘Honeywell, Tucson, Arizona, United States.

Powder bed fusion systems such as direct metal laser sintering (DMLS) provide unprecedented abilities to manufacture complex 3-D parts and structures; however, the process produces unused metal powder that can undergo significant change in chemistry and morphology. The ability to recycle the used powder that is typically found within the build volume and in the overflow compartments requires a thorough chemical and structural analysis in order to determine the extent of reusability. In this context, characterization of virgin powder and used powder for nickel-based and stainless steel based alloys was performed in this work in a rigorous fashion to compare and contrast properties such as composition, particle size distribution and morphology. This information was then used in conjunction with other process parameters (e.g. dose factor, spreader velocity, layer thickness, and laser energy density) to determine conditions that can enable the ready integration of used powder along with virgin powder. Experimental analysis was supported by ANSYS based process modeling in the optimization process, providing a path forward for cost effective additive manufacturing methods.

Spotlight Talk—Effect of Process Parameters on Characteristics of 316 L Stainless Steel Deposited by DED Joyce Miagava1, Raphael G. dos Santos1, Rafael Marzolla1 and Douglas de Alcantara2; Inspec, Sao Paulo, Brazil; "Industrias Romi S.A., Santa Barbara D'Oeste, Brazil.

With the objective of combining advantages of both additive and subtractive manufacturing, several manufacturers are developing hybrid machine tools. Directed energy deposition (DED) method was the additive manufacturing method adopted in these hybrid machines because of the adaptability of the equipment to the milling platform. In order to take advantage of a hybrid platform and obtain a work piece with a good final quality, it is necessary to understand the influence of the additive process parameters. In this work, laser power and scan speed were systematically varied to fabricate 316L test samples to determine the optimal parameters in a recent developed hybrid machining center (Romi DCM 620 5x Hybrid). Optical stereoscopy indicates that the optimal energy input is 50 J/mm². Lower energy inputs are not sufficient to melt the powder and higher energy inputs than 50 J/mm² (with a shield gas flow of 5 L/min) result in porous samples due to an oxidation between deposited layers. Chemical composition was evaluated by Scanning Electron Microscopy coupled to an Energy Dispersive X-ray detector (SEM-EDS) along the height of the samples. Even though an oxidation was observed, EDS results do not reveal any significant Cr and Ni content variation from one measured point to another. Findings of this study will be used as a basis to develop the process with other alloys in hybrid machine-tools.

Spotlight Talk—Corrosive Microstructurization of Nickel-Copper Gas Atomized Powders Stanislau Niauzorau, Aliaksandr Sharstniou and Bruno Azeredo; The Polytechnic School, Arizona State University, Mesa, Arizona, United States.

Microtextured and mesoporous metal alloys, due to its high surface area, have been widely used as fast-charging anodes for Li-ion batteries [1], as metal electrodes for electrolytic methane production [2], and for electocatalysis applications [3]. In recent years, there has been an increasing interest in designing 3-dimensional and hierarchical metal electrodes by integrating wet-chemical methods [4] with 3D printing techniques in order to design and scale topologically complex catalyst systems [5] with increased surface area [6]. In this
study, we examine a specific corrosion-based wet chemistry to induce the microtexturization of gas atomized metal alloy powder as a strategy to introduce surface roughness at microscales to AM feedstock intended for use in selective laser sintering. Microstructurization of NiCu powders was done by electroless chemical etching in 1M HNO3 with the formation of roughened surfaces with RMS at length scales from 20 nm to 5 μm. Additionally, post-processing of the etched microtextured powders in diluted HNO3 reduced the oxygen content from 4 % to 1 % by mass compared to the initial content present in the gas atomized metal powder. Thereby, development of the new controllable chemistry for modification and microtexturing of oxygen-free metal powders may be a promising way for fabrication of the new high surface area metal feedstock for 3D printing of high-surface area electrodes.

References

SESSION CP08.03: Process Optimization and Control I
Session Chair: Dawnielle Farrar-Gaines
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 106 A

1:30 PM CP08.03.01
Fabrication of Robust and Lightweight Hollow Metal Lattice Structures Pawan K. Kanaujia1, Muhammad Azkhairy2, Yee Cheong Lam2 and Chang Quan Lai1; 1Temasek Laboratories, Nanyang, Nanyang Technical University, Singapore, Singapore; 2Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore, Singapore.

In recent years, ultra-lightweight lattices with high stiffness, strength and resilience have been fabricated by coating polymeric microlattices with a thin layer of metal (e.g. Ni, Au) or ceramic (e.g. Al2O3). However, there is limited scalability in the production techniques, which typically involve time consuming processes such as 2-photon polymerization, atomic layer deposition and plasma etching. In this study, we aim to circumvent these limitations by making use of macroscopic stereolithography to 3D print lattices before applying a thin coat of metal through dip coating. The polymeric core of the lattices and binders in the coatings are then removed in a subsequent sintering step at ~1000 °C. The mechanical properties, morphology and chemical composition of the resulting hollow metal lattice are characterized with respect to different sintering duration and temperature. The low cost and easy processing of different shapes allow this technique to be commercially feasible for the mass production of lightweight hollow metallic structures.

1:45 PM *CP08.03.02
Alloy Prototyping Techniques for Powder-Based Additive Manufacturing Eric A. Jagle and Dierk R. Raabe; Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany.

In our research, we focus on designing and developing new alloys specifically for Additive Manufacturing. To avoid the long lead times and significant costs of purchasing bespoke alloy powders, we employ various strategies. In this talk, we present an overview of several of our approaches. First, we bypass powder atomization completely, instead judging alloy processability by laser re-melting coupons made by arc melting. This approach is mainly used for an initial, quick screening of alloy prototyping and allows the identification of compositions that are e.g. prone to hot cracking. Next, we produce alloys by mixing pure element powders in-situ. Using several powder feeders in the DED process, we produce graded specimens that allow quick screening of various alloy compositions in one specimen. This approach is particularly versatile when it is combined with site-specific microstructure analyses by electron microscopy and atom probe tomography. We also process powder mixtures in the L-PBF process, and show how the process needs to be controlled in order to achieve chemical homogeneity. We discuss the limitations of the powder mixing approach, which mainly lie in the limited processability of element combinations with very dissimilar densities and melting temperatures. Finally, we produce our own powders in a self-designed and built EIGA-type lab-scale atomizer. In this talk, we share our lessons learned in preparing very small powder batches for alloy development. The examples presented include steels, Ni-base superalloys and aluminum alloys.

2:15 PM *CP08.03.03
Nanofunctionalization for Additive Manufacturing of Crack-Free High Strength Aluminum Alloys John H. Martin1, Julie Miller1, Brennan Yahata2, Randall Schubert2, Mark O'Masta1, Eric C. Clough1, Jacob Hundley1 and Tobias Schaedler1; 1HRL Laboratories, Malibu, California, United States; 2Materials, University of California, Santa Barbara, Santa Barbara, California, United States.

The ability to 3D print aluminum alloys is an area of high interest due to the wide use of aluminum in the aerospace, automotive, and engineering industries. This range of applications requires an equally broad array of material properties that can be achieved through the various series of aluminum alloys. Recently, nanofunctionalization has been shown to be a viable technique for printing crack-free, high-strength aluminum 7075. Furthermore, this technique is fundamentally applicable to a variety of metal alloys and has now been successfully applied to 2xxx, 6xxx, and 7xxx series aluminum alloys. These alloy systems are historically highly crack susceptible due to their solute contents, freezing ranges, and microstructure evolution during welding, and by extension additive manufacturing. This work demonstrates the success of nanofunctionalization in printing crack-free aluminum alloys belonging to different alloy series, with a specific focus on microstructure evolution and mechanical properties. Attention is also paid to the expansion of the design space around aluminum alloy 3D printing made possible by this technology.

2:45 PM BREAK

3:15 PM CP08.03.04
Developing Metal Matrix Composites via Selective Laser Melting to Optimize Manufacturability and Material Performance Steven Storck, Timothy Montalbano, Salahudin Nimer, Christopher Peitsch and Zachary Ulbig; Johns Hopkins Applied Physics Lab, Laurel, Maryland, United States.

Metal matrix composites (MMC) combine conventional materials to provide highly specialized and otherwise unattainable mechanical performance and material properties such as improved stiffness, strength, hardness, and thermal conductivity. These benefits have had restricted applications, however, because the traditional methods of MMC production, melt casting or powder metallurgy, are limited by high cost and the difficulty of forming desirable geometries. To overcome these limitations we integrated ceramic particles into a metal laser powder bed fusion (L-PBF) additive manufacturing process to enable production of highly complex geometries including topology optimized structures and lattice configurations. In this work, ceramic particles including SiC and TiB2 were introduced into aluminum and steel matrix materials to study the effects on processability in L-PBF
and resulting material properties. In addition, reactive techniques were also explored to form ceramic particles in-situ. Ceramic particles were found to enhance manufacturability during the L-PBF process by altering laser energy absorption and dispersion into the metal powder bed. Relationships between process parameters, microstructure and mechanical performance were elucidated using a combination of X-ray computed tomography, microscopy and hardness testing on samples processed under varying energy conditions. By leveraging the improved manufacturability of metal matrices due to ceramic addition, processing was tailored to result in a greater than 50% reduction in defects and reduced processing energy requirements by up to 56% allowing faster build speeds compared to the conventional metal AM processing. MMCs in complex geometries were demonstrated, and a method for producing metal-to-ceramic gradient materials was developed as another approach to maximize the benefits of both metal and ceramic phases.

3:30 PM CP08.03.05
Optimizing Process Parameters in Selective Laser Melting to Alter Thermal Conductivity  Jacob Simmons, Arad Azizi, Xiaobo Chen, Guangwen Zhou and Scott N. Schifferes; Binghamton University, Binghamton, New York, United States.

The variation in thermal conductivity of 316L stainless steel samples produced with selective laser melting with varying process parameters is investigated in the bulk and in the microscale. A critical scan rate was observed, while holding all other process parameters constant, above which the porosity started to rapidly increase. For the lowest-porosity sample, a local thermal conductivity map was produced using frequency-domain thermoreflectance. The local stainless steel thermal conductivity varied between 10.4 and 19.8 W/m-K. The average thermal conductivity of the thermal conductivity map agrees within measurement uncertainty with flash diffusivity measurements. The reduction in thermal conductivity with increasing scan rate is not fully explained by the porosity. The average measured values are less than conventionally produced bulk 316L due to the unique processing conditions of laser powder bed fusion, which modifies the crystallographic texture and microstructure. Similar trends are expected for all metal laser printed alloys. Complementary SEM and TEM characterizations will be presented.

SESSION CP08.04: Poster Session—Microstructure Analysis and Mechanical Behavior
Session Chairs: Dawnielle Farrar-Gaines and Jennifer Wolk
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

CP08.04.01
Spotlight Talk—Effect of Process Parameters on Characteristics of 316 L Stainless Steel Deposited by DED  Jooyeon Miyaagyu1, Raphael G. dos Santos1, Rafael Marzolla1 and Douglas de Alcantara2; 1Inspec, Sao Paulo, Brazil; 2Industrias Romi S.A., Santa Barbara D’Oeste, Brazil.

With the objective of combining advantages of both additive and subtractive manufacturing, several manufacturers are developing hybrid machine tools. Directed energy deposition (DED) method was the additive manufacturing method adopted in these hybrid machines because of the adaptability of the equipment to the milling platform. In order to take advantage of a hybrid platform and obtain a work piece with a good final quality, it is necessary to understand the influence of the additive process parameters. In this work, laser power and scan speed were systematically varied to fabricate 316L test samples to determine the optimal parameters in a recent developed hybrid machining center (Romi DCM 620 5x Hybrid). Optical stereoscopy indicates that the optimal energy input is 50 J/mm². Lower energy inputs are not sufficient to melt the powder and higher energy inputs than 50 J/mm² (with a shield gas flow of 5 L/min) result in porous samples due to an oxidation between deposited layers. Chemical composition was evaluated by Scanning Electron Microscopy coupled to an Energy Dispersive X-ray detector (SEM-EDS) along the height of the samples. Even though an oxidation was observed, EDS results do not reveal any significant Cr and Ni content variation from one measured point to another. Findings of this study will be used as a basis to develop the process with other alloys in hybrid machine-tools.

CP08.04.02
Spotlight Talk—Corrosive Microstructurization of Nickel-Copper Gas Atomized Powders  Stanislav Niazuoraz, Alaksandr Sharstniou and Bruno Azeredo; The Polytechnic School, Arizona State University, Mesa, Arizona, United States.

Microtextured and mesoporous metal alloys, due to its high surface area, have been widely used as fast-charging anodes for Li-ion batteries [1], as metal electrodes for electrolytic methane production [2], and for electrocatalysis applications [3]. In recent years, there has been a growing interest in designing architected and hierarchical metal electrodes by integrating wet-chemical methods [4] with 3D printing techniques in order to design and scale topologically complex catalyst systems [5] with increased surface area [6]. In this study, we examine a specific corrosion-based wet chemistry to induce the microtexturization of gas atomized metal alloy powder as a strategy to introduce surface roughness at microscales to AM feedstock intended for use in selective laser sintering. Microtexturization of NiCu powders was done by electropolishing chemical etching in 1M HNO3 with the formation of roughened surfaces with RMS at length scales from 20 nm to 5 μm. Additionally, post-processing of the etched microtextured powders in diluted HNO3 reduced the oxygen content from 4% to 1% by mass compared to the initial content present in the gas atomized metal powder. Thereby, development of the new controllable chemistry for modification and microtexturing of oxygen-free metal powders may be a promising way for fabrication of the new high surface area metal feedstock for 3D printing of high-surface area electrodes. References  

CP08.04.03
Spotlight Talk—Optimization of Process Parameters for Additive Manufacturing Using Recycled Metal Powder  Susanna J. Castillo1, Anna K. Hayes1, Krishna Muralidharan1, Gregory Colvin2, B.G. Potter1 and Melissa Bush1; 1University of Arizona, Tucson, Arizona, United States; 2Honeywell, Tucson, Arizona, United States.

Powder bed fusion systems such as direct metal laser sintering (DMLS) provide unprecedented abilities to manufacture complex 3-D parts and structures; however, the process produces unused metal powder that can undergo significant change in chemistry and morphology. The ability to recycle the used powder that is typically found within the build volume and in the overflow compartments requires a thorough chemical and structural analysis in order to determine the extent of reusability. In this context, characterization of virgin powder and used powder for nickel-based and stainless steel based alloys was performed in this work in a rigorous fashion to compare and contrast properties such as...
composition, particle size distribution and morphology. This information was then used in conjunction with other process parameters (e.g. dose factor, spray velocity, layer thickness, and laser energy density) to determine conditions that can enable the ready integration of used powder along with virgin powder. Experimental analysis was supported by ANSYS-based process modeling in the optimization process, providing a path forward for cost-effective additive manufacturing methods.

**CP08.04.04**

Study on Thermal Stability of Nanocrystallized Inconel 718 Induced by Electropulsing Assisted Ultrasonic Surface Rolling Process

Zhiyuan Sun and Bo Li; Tsinghua University, Beijing, China.

The thermal stability of nanocrystallized Inconel 718 induced by ultrasonic surface rolling process (USRP) and electropulsing assisted ultrasonic surface rolling process (EP-USRP) in the range of 650-800 degrees Celsius was carefully investigated in the present work. The results indicated that EP-USRP specimens exhibited excellent thermal stability both in microhardness and microstructure below 750 degrees Celsius, which is higher than the normal service temperature (650 degrees Celsius) of Inconel 718. After a short time (1 h) heat treatment, the Vickers microhardness of USRP specimens and EP-USRP specimens still displayed gradient distributions with the surface value of EP-USRP specimens higher than USRP specimens. The microstructure of severe plastic deformation layer of EP-USRP specimen was thermally stable below 750 degrees Celsius. In addition, even after 10 h heat treatment, EP-USRP specimens still showed higher stability in microhardness and microstructure than USRP specimens below 750 degrees Celsius. For EP-USRP specimens at high temperatures, the more amounts of homogeneously dispersing nano-sized precipitates and the finer grains are likely the primary reasons for the observed phenomena. That is, the interaction between ultra-refined grains and nano-sized precipitates provides pinning forces and hence could endow the material with good thermal stability.

**CP08.04.05**

The Interplay of Metals with Carbon and Boron Nitride Nanotubes

Christoph Rohmann1,2 and Michael Zwolak2; 1IREAP, University of Maryland, College Park, Maryland, United States; 2PML, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The integration of nanofibers into the lattice of metals has been a long-standing goal, mainly due to the gained superior properties. Although intensive research has been undertaken to incorporate carbon based materials into metals, such as carbon fibers of carbon nanotubes (CNTs), the results have shown that these materials tend to dissolve and form undesired carbides, which are detrimental to the composite.

A viable alternative is presented in the form of boron nitride nanotubes (BNTNs), a structural analog to CNTs. Thus formed BNTN-metal-matrix-composite (BNTN/MMC) material is expected to be light weight with an improved elastic modulus, strength, toughness and thermal conductivity, while offering additional benefits in the form of a high oxidation temperature, corrosion-free and radiation shielding capabilities. We will present the results of quantum chemical calculations, of the binding strength and geometry of a variety of metals with carbon and boron nitride nanotubes with special focus on the integration of BNTNs into an Al, Ti and Cu metal matrix.

**CP08.04.06**

An Electrochemical 3D Printer for Room-Temperature Direct Additive Manufacturing of Multiple Metals

Matteo Chiesia1, Marco Stefancich2, Thor Sverre Minnesjord1 and Harry Apostolides1; 1Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Dubai Electricity and Water Authority, Dubai, United Arab Emirates; 1Fluid Metal 3D, Skien, Norway.

The current paradigm of metal 3D printing, based on laser sintering of metal powder, has revolutionized industrial prototyping and even manufacturing of custom parts. However, this approach, relying on high-temperature processes and expensive equipment, is poorly suited to smaller-scale applications such as the development of electronic components. We present an electrochemical 3D printer that uses localized electrodeposition of metal to directly print 3D structures at room temperature. The presented instrument consists of a 100µm-scale nozzle mounted on a 3-axis movement system similar to a conventional 3D printer, with an electrical potential applied between the nozzle and the build plate. An electroplating solution is circulated through the system so that emerges from the nozzle as a high-speed jet before impinging on the build plate, where metal ions are reduced onto the surface by electrodeposition. The jet allows the system to achieve deposition speeds many times higher than conventional electrodeposition methods by disrupting the diffusion-limited boundary layer at the deposition surface. We describe the physics of the jet-assisted electrodeposition process and derive the relationships between various parameters including current, jet speed, composition of the print solution, and print speed. Particular attention is given to the current-voltage characteristic and its relationship to jet speed; the limiting current for the deposition process and how it can be enhanced; and the impact of high current densities on deposition quality. Consideration is given to the fluid dynamics of the system, and importance of the nozzle geometry in determining the properties of the jet. We present detailed results for the printing of copper from a Cu/H2SO4 solution, preliminary results for printing nickel, and the potential for the use of other metals with different deposition solutions. We offer a detailed characterization of printed Cu, proving that the deposited metal is of high purity and density, with the expected thermal, mechanical and electrical properties. We demonstrate the printing of geometries, including freestanding 3D structures without supports, that are beyond the capabilities of conventional 3D printers; multi-material 3D printing capability; and the ability to print on non-conductive substrates, overcoming a key limitation of standard electrodeposition methods. We furthermore explore the printer’s capability as a reversible deposition/etching system, allowing for additive and subtractive processes to be combined in a single run. A promising area of application is in the prototyping of electronic circuit boards. We demonstrate how the electrochemical printer can rapidly print circuit boards, either in subtractive mode by locally etching the Cu coating from a conventional PCB, or in additive mode by directly printing conductive electrical connections onto a non-conductive substrate.

**SESSION CP08.05: Applications and Next Generation AM**

Session Chairs: Dawnielle Farrar-Gaines and Jennifer Wolk

Wednesday Morning, April 24, 2019

PCC West, 100 Level, Room 106A

8:45 AM CP08.05.01

Reactive 3D Printing of Semiconductor GaN

Jarod C. Gannon, Michael Presley, Timothy Montalbano and Steven Storck; Johns Hopkins University Applied Physics Lab, Laurel, Maryland, United States.

We have demonstrated a reactive additive manufacturing process that results in the formation of single-crystal semiconductor GaN. Printed GaN regions have been fabricated through the presented method with a single GaN(002) peak present in θ/2θa-omega XRD scans, indicating a single orientation crystal film. X-ray diffraction and energy dispersive spectroscopy have been used to confirm full conversion of reactive precursors to form GaN with no remaining precursors present in the crystal structure. Through this method, single-crystal GaN films up to 1µm in thickness have been fabricated with crystal growth rates that are orders of magnitude higher than standard semiconductor synthesis methods. We will outline the semiconductor printing method as well as the challenges associated with this process including print resolution, crystal orientation and impurity control.

9:00 AM CP08.05.02

Texture in Electron Beam Melted Tungsten for Fusion Power

Elizabeth A. Ellis1, Michael M. Kirk1, Chase B. Joslin1, Lauren M. Garrison2, Yutai Katoh2 and Ryan R. Dehoff1; 1Manufacturing Demonstration Facility, Oak Ridge National Laboratory, Knoxville, Tennessee, United States; 2Nuclear Materials Science and Technology, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The application of additive manufacturing (AM) techniques to problems in fusion power provides an exciting opportunity to advance both technologies. Small plasma-facing components such as divertors and armor tiles for tokamak power plants are required to withstand extremely high heat and neutron fluxes, and must therefore be manufactured from difficult-to-machine materials such as tungsten. Additive manufacturing allows fabrication of components in new geometries out of new materials, with a high degree of control over component microstructure. Microstructure is particularly important for small plasma-facing tungsten components, where intergranular fracture is a common failure mode and grain boundary placement must therefore be carefully considered. To be discussed is AM of tungsten components for fusion applications via electron beam melting (EBM). EBM offers a high degree of control over heat input, including the possibility of site-specific microstructure control by means of a point melt scan strategy. Spot melting strategies were...
Printability of CrMnFeCoNi High Entropy Alloy envisioned. Vibro-finishing was found to be an efficient post-processing method for fatigue life improvement. X-ray tomography (voxel size of 0.75 µm) also involving ex-situ fatigue crack propagation. When excessive roughness is the cause of fatigue failure, other post-treatments may be implemented. This post-treatment could be applied locally in regions of stress concentration more prone to fatigue failure. A significant improvement in fatigue life was inadmissibly low level. In this sense, friction stir processing (FSP), a post-treatment method derived from friction stir welding that has been proven useful in Al cast material, was sometimes be unavoidable to improve the fatigue life. Hot isostatic pressing (HIP) yields very satisfactory results for Ti based AM alloys and is routinely applied in this industry. The optimisation of process parameters has already been extensively studied for bulk AlSi10Mg and is provided by the machine manufacturers. Now, post-treatments may sometimes be unavoidable to improve the fatigue life. Hot isostatic pressing (HP) yields very satisfactory results for Ti based AM alloys and is routinely applied in this industry, but the typical 500°C/100MPa/2h cycle used for AlSi10Mg cast parts increases ductility, but also ruins the SLM fine microstructure, depleting mechanical strength to an inadmissibly low level. In this sense, friction stir processing (FSP), a post-treatment method derived from friction stir welding that has been proven useful in Al cast material, was implemented. This post-treatment could be applied locally in regions of stress concentration more prone to fatigue failure. A significant improvement in fatigue life was demonstrated on polished bulk samples. This is attributed to the positive impact of FSP allowing to eliminate large porosities. These porosities were studied by 3D synchrotron X-ray tomography (voxel size of 0.75 µm) also involving ex-situ fatigue crack propagation. When excessive roughness is the cause of fatigue failure, other post-treatments may be envisioned. Viro-finishing was found to be an efficient post-processing method for fatigue life improvement. Contrarily to the bulk structures mentioned above, for thin structures (typically a couple of 100µm of µm) the contouring strategy plays a dominant role on the roughness and sub-surface porosities. The surface roughness of a large variety of processed parts was compared and their origin discussed. The sub-surface porosities were studied by laboratory X-ray tomography. The post-treatments mentioned previously may cause excessive deformation of very thin samples. Thus, a contour strategy optimisation is a first step towards their fatigue resistance improvement.

Printability of CrMnFeCoNi High Entropy Alloy Son Pham; Materials, Imperial College London, London, United Kingdom.

The printability of CoCrFeMnNi high-entropy alloy in laser powder bed fusion is evaluated in this study. A single-track of the alloy was examined to study the solidification microstructure in rapid cooling. Subsequently, multi-layer builds were fabricated with different scanning strategies to study the consolidation and how the microstructure evolves in the subsequently repeated deposition. The present study shows that CoCrFeMnNi has excellent printability with high consolidation and excellent strength. Both monotonic tension and cyclic loading were carried out to study the plasticity and fatigue performance of the alloy additively manufactured with varying scanning strategies.

Transients in Plastic Instabilities During Thermo-Mechanical Reversals in Metal Additive Manufacturing Sabina C. Kumar1,2, Peyyush Nandwana2 and Sudarsanam S. Babu1,2; 1University of Tennessee, Knoxville, Tennessee, United States; 2Oak Ridge National Laboratory, Knoxville, Tennessee, United States.

Additive Manufacturing (AM) literature has shown that the final properties of AM fabricated components are influenced by the complex interactions between geometry, process parameters and alloy chemistry. These interactions can be traced back to spatial and temporal variations of thermal and mechanical signatures (i.e., T \{x, y, z, time\}). These variations affect all phenomena starting from defect formation, solidification grain structure, solid state transformation and accumulated plastic deformations. Although the above changes are similar to welding, we do observe large reversals of these signatures in AM because of the spatial and temporal transients brought about by the rapid changes in energy delivery modes. The evolution of residual stress distribution due to the non-uniform accumulation of plastic strains within the build is a common concern among all different methods of AM of metallic parts. This plastic strain evolution during repeated thermal cycling is brought about by macro scale changes in the thermal gradients, changes in thermal expansion-coefficient and crystallographic changes between phases and constitutive stress-strain properties. The fundamental response of metals and alloys that undergo solid state phase transformations while being subjected to alternating temperature (above and below the instability temperature) and stress (elastic and plastic) have not been measured before and forms the basis for the current research. The model alloy chosen to understand this complex behavior is Ti – 6Al – 4V. Thermomechanical processing of α/β titanium alloys are largely based on the β → α + β transformation on cooling. It is well known in titanium literature that α plates usually maintain a specific orientation relationship with the β matrix, referred to as the Burgers orientation relationship which is (101)β // (0001)α, and [-111]β // [2110]α. There are 12 crystallographically equivalent orientation variants of the α phase within a single β grain. Each of the variants has a different transformation strain, different degrees of elastic self-accommodation when in contact with each other and different interfacial energies when in contact with grain boundaries. Phase field simulations have shown that this leads to variant selection (i.e., some variants appear more frequently than the other) accompanying a precipitation which then led to the formation of a transformation texture or microtexture. Since the α phase has highly anisotropic in its physical and mechanical properties, this evolving microtexture will determine to a large extent the response of the alloy towards thermo-mechanical cycling. Thus, it would be detrimental if only a single or few variants of alpha percolate the whole matrix. For our research, three different scan strategies (a line scan and 2 types of spot scan) were incorporated to build 15 x 15 x 25 mm cubes, in order to get a variation of thermal gradients across the build. Initial characterization of the as fabricated Ti – 6Al – 4V cube of the line scan sample, using back scattered electrons with SEM, has shown that different α morphology has precipitated along either side of the prior β grain boundary. On one side we see a basket-weave type α while on the other side we see a fine lath type α. Further EBSD analysis has shown that the texture of α is different at the top of the cube and the bottom of the cube. Our work here illustrates the response of this α/β Ti-alloy to thermo-mechanical cycling with proper registration of boundary conditions to simulate typical thermal
cycling conditions during AM of metals. Based on the literature, we hypothesize that the response will be dictated by redistribution of global stress/strain in between the rapidly changing phase fractions (i.e., HCP - α and BCC - β). A semi-analytical heat conduction model was used to predict the transient heat transfer behavior during powder bed metal AM. Using this model we can register proper boundary conditions.

11:00 AM *CP08.06.04
Laser Beam Melting of Large-Scale Ti-6Al-4V Parts—Increasing Productivity and Reducing Residual Stresses Dirk Herzog1,2, Katharina Bartsch1,2, Kai-Fabian Schenk1 and Claus Emmelmann1,2; 1Institute of Laser and System Technologies, Hamburg University of Technology, Hamburg, Germany; 2Fraunhofer Research Institute for Additive Manufacturing Technologies IAPT, Hamburg, Germany.

Parts made of the titanium alloy Ti-6Al-4V make up for about 50% of the titanium market. The material is today widely used for lightweight applications, e.g. in the aerospace industry. Additive Manufacturing can significantly contribute to lightweight design due to its high design freedom and only very few manufacturing restrictions. Therefore, lightweight Ti-6Al-4V parts represent some of the most promising industrial business cases for Additive Manufacturing these days, such as the brake caliper of Bugatti Chiron and brackets holding the flight crew rest compartment in the Airbus A350 produced by laser beam melting. Part integration, where larger assemblies of parts are integrated to one additively manufactured part, has shown to save additional costs in industrial applications. This leads to the desire to print ever larger parts through Additive Manufacturing technologies such as laser beam melting.

Large scale parts, with dimensions exceeding 0.3 m in at least one orientation, however feature increasing problems from residual stresses during the process. As a result, a high amount of support structures is needed to handle the stresses, which in turn causes high amount of post processing. Depending on the exact geometry, a first-time right production cannot be guaranteed or the parts are simply not manufacturable. Taking into account the comparatively low productivity of today’s laser beam melting machines it is also less economical to produce large scale parts.

In this context, a new approach for laser beam melting is proposed. Instead of optimising process parameters with regard to the highest possible density, the process parameters are optimised to yield the highest possible speed and the lowest possible residual stresses while maintaining a density above 95%. It can be shown that parts fulfilling these criteria may be fully densified through hot-isostatic pressing in a following step. The presentation will look at the differences in residual stresses in test specimens as well as in a large scale part, on the resulting microstructures, as well as on the economics of the process, which profits from a ~60% speed gain and thus reduced machine time.

SESSION CP08.07: Characterization—Microstructure Analysis and Mechanical Behavior II
Session Chair: Dawnielle Farrar-Gaines
Wednesday Afternoon, April 24, 2019
PCC West, 100 Level, Room 106 A

1:30 PM *CP08.07.01
Qualification of Additive Manufactured Components—Integration of Modeling, Measurement and Manufacturing Processes Sudarsanam S. Babu1,2; 1University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2Manufacturing Demonstration Facility, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Additive manufacturing (AM) enables design and production of structural metallic components with complex geometries. Recent work has shown that, in addition to complex geometries, site-specific microstructures can be achieved through careful control of processing condition at every layer. These advances are made by leveraging the similarity of physics between welding and AM processes. The interactions between boundary conditions imposed by component geometry, wide variations of thermal signatures brought about by mode of energy delivery, and composition of the alloys can be used for qualification of AM components. This overview presentation will discuss pragmatic integration of recent innovations related to modeling, measurements and manufacturing methodologies with case studies from titanium and nickel alloys.

The first part of the paper will focus on the modeling tools for topology optimization of component geometry, process modeling of heat and mass transfer, solidification and solid-state transformations, plastic deformations, residual stress, distortion and performance of the components. The process flow involved in linking all these discrete modeling tools, challenges and future directions will be outlined with published examples from both welding and additive manufacturing. The second part of the paper will focus on the in-situ characterization of process and also correlation of the same to evolution of defects and microstructure in titanium and nickel alloys. The third part of the paper will focus on case studies involving both computational modeling and in-situ characterization to arrive at strategies for qualification of the AM components. Finally, this paper will also focus on some of the unresolved questions related to stability of interfaces between liquid and solid, solid and solid, as well as, deformation conditions within the solid during additive manufacturing and approaches to address the same.

2:00 PM *CP08.07.02
Rapid Development of Mechanical Models for Additively Manufactured Materials Michael Presley, Phillip Koshute, John Skotwinski and Christopher Peitsch; JHU/APL, Laurel, Maryland, United States.

Material property variance in powder bed fusion processes is heavily influenced by both pore like defects and microstructure, complicating extension of traditional microstructural models to optimization and qualification of AM materials. In addition while traditional A/B basis testing approaches capture variability in an ideal process, they do not allow prediction of properties for local variations in laser power, melt pool size, or powder layer thickness. As in-situ monitoring becomes more wide spread the ability to predict the impacts of these common deviations will be vital to process certification. In this work we demonstrate how simple nonlinear regression techniques including neural networks and random forests can be used to quickly model the influence of lack of fusion defects on mechanical properties of Ti64. These models can then be leveraged to predict experimental regions of interest to minimize the number of high cost experiments needed for more in depth analysis. 128 vertical Ti64 ASTM ES tensile bars were produced using different laser processing parameters on a Renishaw AM400. Four parameters were varied using a Latin hyperecube sampling approach: laser power, hatch distance, point distance, and exposure time. Test outputs were modulus, ductile vs. brittle fracture, yield strength, and ultimate tensile strength. Given a set of processing conditions, predictive models were developed that could successfully predict ductile vs. brittle fracture at 84% accuracy, and yield strength within 90%. Five samples selected to span the entire mechanical output range were further analyzed using X-Ray computed tomography to evaluate the degree of lack of fusion cracking and explain underlying microstructural basis for varying mechanical behavior. Going forward, these models can be used both to estimate process variability and selectively tailor AM parts for desired mechanical performance.

2:30 PM BREAK

3:30 PM CP08.07.03
Microstructural Analysis and Mechanical Behavior of a High Entropy Alloy Produced with Selective Laser Melting (SLM) Nikole Kucza1, Michelle A. Othon1, Mallikarjun Karadge1, Daniel Ruscito1, Cole Crawford1, Keith Lauria1, Richard J. Blair1, Raul Rebak1, Martin Morra1 and Kosuke Kuwabara1; GE Global Research, Niskayuna, New York, United States; 2Global Research & Innovation Technology Center GRIT, Hitachi Metals Ltd., Kumagaya, Japan.

A CoCrFeNiTiMo-based high entropy alloy (HEA) powder was used to successfully print near-net-shape hardware and test-blocks for examination of selective laser melting (SLM) materials properties. Additive manufacturing (AM) has enabled the manufacture of this difficult-to-process material. By simultaneously exploiting the fast cooling rate of industry. Additive Manufacturing can significantly contribute to lightweight design due to its high design freedom and only very few manufacturing restrictions. Therefore, lightweight Ti-6Al-4V parts represent some of the most promising industrial business cases for Additive Manufacturing these days, such as the brake caliper of Bugatti Chiron and brackets holding the flight crew rest compartment in the Airbus A350 produced by laser beam melting. Part integration, where larger assemblies of parts are integrated to one additively manufactured part, has shown to save additional costs in industrial applications. This leads to the desire to print ever larger parts through Additive Manufacturing technologies such as laser beam melting.

Large scale parts, with dimensions exceeding 0.3 m in at least one orientation, however feature increasing problems from residual stresses during the process. As a result, a high amount of support structures is needed to handle the stresses, which in turn causes high amount of post processing. Depending on the exact geometry, a first-time right production cannot be guaranteed or the parts are simply not manufacturable. Taking into account the comparatively low productivity of today’s laser beam melting machines it is also less economical to produce large scale parts.

In this context, a new approach for laser beam melting is proposed. Instead of optimising process parameters with regard to the highest possible density, the process parameters are optimised to yield the highest possible speed and the lowest possible residual stresses while maintaining a density above 95%. It can be shown that parts fulfilling these criteria may be fully densified through hot-isostatic pressing in a following step. The presentation will look at the differences in residual stresses in test specimens as well as in a large scale part, on the resulting microstructures, as well as on the economics of the process, which profits from a ~60% speed gain and thus reduced machine time.
Additively manufactured metallic materials are known to exhibit high levels of micro-structural inhomogeneity, defects and residual stress. These undesirable features originate from the non-equilibrium manufacturing process involving very high spatial and temporal gradients in temperature. As a result, these materials have defects spanning multiple length-scales and suffers from drastic loss in ductility and toughness. The conventional approach to mitigate this issue is to perform thermal treatment, such as annealing or hot isostatic pressing.

In this study, we explore an alternate route that is non-thermal in nature. The selected material was Ti-6Al-4V alloy manufacture using laser-based, directed energy- deposition system. Thin section (50-150 microns) specimens were prepared to be used in an experimental setup that allows us to study the synergy of electrical current and tensile strain instead of temperature. Our approach involves passing electrical current in the specimens at much lower current density than the electro-migration damage limit. This directly causes Joule heating, which is eliminated by both passive and active heat removal techniques to keep the specimen temperature at or near ambient conditions. We then study the role of mechanical strain on the grain growth at room temperature. The experiments were performed inside a SEM with Electron back scattered diffraction (EBSD) for in-situ characterization. For electrical tuning below 150 °C, the fraction of kernels with misorientation less than 2° increased to ~70% and 99%, respectively; whereas the kernels with misorientation greater than 4° dropped to ~9% and 0%, respectively. These changes are with respect to the as-deposited specimen materials, which is a clear evidence of the reduction/elimination of residual strain via electric field annealing.

4:00 PM CP08.07.05
Evaluation of a Learning Tool for In Situ Monitoring of Metal Additive Manufacturing Brent Valle1, Karel Lietaert1, Fatania Antler2, John Newman2, Erik Xiao2, Sam Crock3 and Jonas Van Vaerenbergh1; 13D Systems, Leuven, Belgium; 2KLA Tencor, Milpitas, California, United States.

This study describes a multi-channel in-situ monitoring system developed to better understand defect formation signatures in metal additive manufacturing. Three high-speed imaging modes coupled with an image computer capable of processing and storing these data streams allowed an examination of defect formations signatures and mechanisms. It was found that defects later detected in x-ray computed tomography (CT) scans were related to regions with anomalous heat signatures and powder bed morphology. Automated defect detection algorithms based on these defect signatures captured 80% of defects greater than 300µm.

4:15 PM CP08.07.06
Nanoindentation Based Investigation of Additively Manufactured Inconel 718 at High Temperature Tyler Palma1, Ali Beheshti2 and Keivan Davami2; 1Lamar University, Beaumont, Texas, United States; 2George Mason University, Fairfax, Virginia, United States.

Advanced alloy materials are frequently utilized in applications comprising extreme conditions such as high temperatures or corrosive materials. Nickel chromium based alloys are one such group which is commonly used in industries including jet engine manufacturing, thermal and nuclear power generation, and petroleum engineering, and thus it is crucial to learn how reliably they operate at various scales and in different conditions. There is broad interest in further understanding the mechanical behaviors and reliability of these advanced alloys in settings which more closely mimic those in which they are applied, particularly pertaining to how they are affected at the nano and microscales. This work focuses on the experimental investigation of one such alloy, Inconel 718, which has been fabricated by means of additive manufacturing, and the dependence of its mechanical properties on temperatures ranging from –200 °C up to 800 °C. Advanced nanoindentation methods are used to characterize mechanical and tribological properties, including tribological responses, creep behaviors, and the variation of cracking thresholds for the determination of fracture toughness. Previous work has shown that mechanical properties in such alloys can be altered by variation of their environment, and it is reported that for large changes in temperature there are noticeable effects in the basic mechanical properties such as hardness and elastic modulus, which was seen to decrease by nearly 30 % at increased temperature, as well as more vital qualities like fracture behavior. It was concluded that the fracture toughness of additively manufactured Inconel 718 at room temperature is approximately 70 MPa-m²/2, and the cracking threshold load is variable and is dependent on the material temperature.

SYMPOSIUM CP09

Mathematical Aspects of Materials Science—Modeling, Analysis and Computations
April 23 - April 26, 2019

Symposium Organizers
Patricia Bauman, Purdue University
Jose Carrillo, Imperial College London
Maria Emelianenko, George Mason University
Dmitry Golovaty, University of Akron

Symposium Support
Army Research Office

* Invited Paper

SESSION CP09.01: Modeling, Analysis and Simulations of Soft Matter
Session Chairs: Patricia Bauman and Dmitry Golovaty
Tuesday Morning, April 23, 2019
PCC West, 100 Level, Room 106 B

10:30 AM CP09.01.01
Electrically Driven Three-Dimensional Solitary Waves as Director Bullets in Nematic Liquid Crystals Oleg D. Lavrentovich1, Bing-Xiang Li2, Rui-Lin Xiao2 and Sergij Shyanovskii; 1Advanced Materials and Liquid Crystal Institute, Department of Physics, Kent State University, Kent, Ohio, United States; 2Advanced Materials and Liquid
Electric field induced collective reorientation of nematic liquid crystal molecules is of importance for fundamental science and practical applications. This reorientation is either homogeneous over the area of electrodes, as in displays, or periodically modulated, as in electroconvection. The question is whether spatially localized three-dimensional solitary waves of molecular reorientation could be created. Here we demonstrate that the electric field can produce particle-like propagating solitary waves representing self-trapped “bullets” of oscillating molecular director. The oscillations are of the same frequency as the frequency of the driving electric field. These director bullets lack fore-aft symmetry and move with a very high speed perpendicularly to the electric field. They can move either parallel or perpendicularly to the initial alignment direction. The solitons moving perpendicularly to the director have been described in recent publication by our research team, see B.-X. Li et al, Nature Communications, volume 9, 2912 (2018). The bullets are true solitons that preserve spatially-confined shapes and survive collisions. The solitons are topologically equivalent to the uniform state and have no static analogs, thus exhibiting a particle-wave duality. Their shape, speed, and interactions depend strongly on the material parameters, which opens a door for a broad range of future studies. The work is supported by NSF DMREF grant DMS-1729509.

11:00 AM *CP09.01.02 Spherical Particle in Nematic Liquid Crystal Under an External Field—The Saturn Ring Regime Stan Alama1; Lin Brennard1 and Xavier Lamy2; 1Math and Stats, McMaster University, Hamilton, Ontario, Canada; 2Institut de Mathématique, Univ de Toulouse Paul Sabatier, Toulouse, France.

We consider a nematic liquid crystal occupying the exterior region in $\mathbb{R}^3$ outside of a spherical particle, with radial strong anchoring. Within the context of the Landau-de Gennes theory, we study minimizers subject to an external field, modelled by an additional term which favors nematic alignment parallel to the field. When the external field is high enough we obtain a scaling law for the energy. The energy scale corresponds to minimizers concentrating their energy in a boundary layer around the particle, with quadrupolar symmetry. This suggests the presence of a Saturn ring defect around the particle, rather than a dipolar director field typical of a point defect. This is joint work with Stan Alama (McMaster) and Xavier Lamy (Institut de Mathématique, Université de Toulouse Paul Sabatier.)

11:30 AM *CP09.01.03 Chromonic Liquid Crystals and Bacteriophage Viruses Maria-Carme Calderer; University of Minnesota, Minneapolis, Minnesota, United States.

Lyotropic Chromonic Liquid Crystals (LCLCs) consist of disk, plank-like molecules with rigid cores and ionic groups in the periphery, that undergo phase transitions from isotropic to hexagonal columnar phases as the concentration increases. The chromonic liquid crystal family embraces a very broad range of materials ranging from nucleotides, DNA and RNA to dyes and food additives (e.g. Sunset Yellow), proteins and pharmaceutical products. With the addition of condensing agents, such as pEG and spermine, the columns are found to aggregate into faceted, elongated toroidal clusters, with a typical size of 200 microns, with pressures of the order of 0.1 atmospheres. Double-stranded DNA in free solution also forms toroidal aggregates in the presence of condensing agents, but with cluster sizes about 100,000 times smaller than those formed by DSCG. An important class of chromonic aggregates are those formed by bacteriophage viruses as their dsDNA spoils into an ordered structure inside the capsid. Typical viral capsids measure about 50 nm and sustain pressures of the order of 30-60 atmospheres. These large pressure values result from the competition of the high bending resistance of the DNA filament with the repulsive electrostatic force between neighboring strands.

The increased awareness of the relevant role that bacteriophage viruses may have in controlling bacterial infection processes motivates our study of such systems. In this presentation, I will discuss two models of chromonic cluster formation, one purely mechanical and a more comprehensive second model that accounts for the permeability of the capsid and changes in its polyelectrolyte environment.

SESSION CP09.02: Mathematical Methods in Design of New Materials and Applications
Session Chairs: Patricia Bauman and Dmitry Golovaty
Tuesday Afternoon, April 23, 2019
PCC West, 100 Level, Room 106 B

1:30 PM *CP09.02.01 The Direct Conversion of Heat to Electricity Using Ferroelectric Oxides Richard D. James; University of Minnesota, Minneapolis, Minnesota, United States.

We describe recent progress on materials and devices for the direct conversion of heat to electricity applicable to the small temperature difference regime, 10-200 C. We are pursuing an idea based on the use of first order phase transformations in epitaxial ferroelectric oxide films. It is a “direct” method in the sense that there is no separate electrical generator. We develop a mathematical theory of this method and apply it to the design of the materials and devices and the analysis of cycles. We compare theoretical predictions and the behavior of a prototype under cyclic heating/cooling. These devices provide interesting possible ways to recover the vast amounts of energy stored on earth at small temperature difference. They move heat produced by natural and man-made sources from higher to lower temperature and therefore contribute negatively to global warming.

2:00 PM *CP09.02.02 Design of Nematics Through Colloidal Homogenisation Arabir D. Zarnescu1,2; 1,2Basque Center for Applied Mathematics, Bilbao, Spain; 1“Simion Stoilow” Institute of Mathematics, Bucharest, Romania.

We work within the framework of Landau-de Gennes variational theory of nematics and show how one can obtain from a given nematic material, say A, a desired a posteriori prescribed nematic material, say B, through a suitable homogenisation procedure of suitably chosen (depending on A and B) colloidal inclusions. This is joint work with Giacomo Canevari (Basque Center for Applied Mathematics).

2:30 PM *CP09.02.03 Hidden Variables and Internal Scales in Composite Materials Elena Cherkaeve; University of Utah, Salt Lake City, Utah, United States.

Formulations of problems governing the behavior of the fields in composite materials and heterogeneous media with microstructure often contain internal or hidden variables that model the influence of the processes on the microstructural level. The talk discusses a set of internal variables that are naturally related to the structure of a composite. These hidden variables determine the characteristic internal scales in the composite corresponding to the microlevel processes of different characteristic wavelengths. The parameters of composite’s microgeometry are incorporated into the internal variables through the spectral measure in the Stieltjes analytic representation of the effective properties of the composite; this spectral measure determines the equations for the evolution of the internal variables. The spectral measure contains all information about the geometry of the media on the microscale and links it through the hidden variables to the behavior of the material on the macroscale.

3:00 PM BREAK

3:30 PM CP09.02.04 Flow Effects in High-Frequency Homogenization of Porous Media in Electromagnetic Heat Exchangers Hrut Tilley; Vadim V. Yakovlev and Joseph M. Gaone; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Electromagnetic (EM) heat exchangers are devices which absorb EM radiation converting it into thermal energy to do mechanical work. Applications involving both solar and microwave energy have garnered increasing attention but have yet to utilize the potential benefits of short-wave interactions with the local geometry when the wavelength is comparable to a material’s microstructure. It has been shown for a three-layer laminate that Bragg resonance occurs in this case, and this resonance can be used to control steady
state temperature and thermal runaway effects. We investigate these effects in a mathematical model approximating a porous medium for use in a heat exchanger. Classical homogenization methods average over the microscale to obtain a macroscopic description of the material, however, they are incapable of describing short-wave behavior. High-frequency homogenization methods have been developed, but they are restricted to cases incompatible with modeling heat exchangers, such as assuming a lossless medium, spatially uniform dielectric constants, and reducing Maxwell’s equations to the Helmholtz equation. Here we develop a high-frequency homogenization technique that relax these assumptions, considering a laminate geometry composed of alternating layers of lossy dielectric material and lossless fluid channels in the homogenization limit. The presence of flow in the three-layer laminate is shown to induce sharp, but controlled, increases in the spanwise average temperature. The effects of slow flow along with thermal transport throughout the effective medium are also discussed.

3:45 PM CP09.02.01
Predicting Dynamic Properties of Computer Designed Metal-Organic Frameworks by Deep Learning Weiwei Zhang1, Chengxi Yang2, Matthew Campbell2 and Alex Greenay1, 2 Materials Science and Engineering, University of California, University of California, Riverside, Riverside, California, United States; 3 School of Mechanical, Industrial, & Manufacturing Engineering, Oregon State University, Corvallis, Oregon, United States.

Metal-Organic Frameworks (MOFs) are found to be one of the best materials for gas storage because of their large surface area and high flexibility. MOFs are compound with metallic nodes and organic linkers. We have developed an automated system to design the linkers for MOF by computer. This approach formally encompasses a design space of molecules that is astronomically large and beyond the brute force exploration by computer. In order to accelerate the search of this space, we have tested machine learning methods for forecasting several different forms of linker molecules' mechanical behavior from the structure. Two systems representing the structures, high order geometric moments and blurred voxelization, were taken as well-performed features for deep learning artificial neural networks to be trained for dynamic, physics and chemical properties with high accuracy. The capability of predicting the evaluation results rather than experiment or simulating calculation will accelerate the search of new materials in a vast design space. The result shows that with the system size grows, the prediction will be more accurate.

4:00 PM CP09.02.02

Dislocations are fundamental defects that mediate plastic deformation in metals. Studies of dislocation core structures have relied on a variety of coupling techniques to manage the far-field strain fields; one very successful approach for pure materials has been the flexible boundary condition method based on the lattice Green function. However, the treatment of dislocations in random alloys with atomic-level detail is significantly more challenging due to the range of environments: both local relaxation of atoms as well as the long-range field must be considered, and there is lack of efficient and accurate approaches to treat both. Here, we describe a method to calculate the dislocation core of non-dilute BCC binary random alloy efficiently by combining the first-principle calculation with an optimized multicomponent Gaussian Approximation Potential (GAP) specially designed for use with flexible boundary conditions. We use density functional theory to compute the energies, forces, elastic constants and force constants of BCC-based Ti-Mo ordered and disordered structures at zero and finite temperatures. This provides the database for our optimized Ti-Mo GAP model that accurately reproduces first and second derivatives of energies for a range of structures relevant to a dislocation. The GAP model relaxes a large dislocation geometry with random chemical species, and then the force constants for the full dislocation are computed and the lattice Green function constructed. This initial step is crucial, as flexible boundary condition methods leave far-field forces unchanged through the relaxation process. Finally, boundary conditions can be used with density-functional theory to compute the core structure of a random alloy.

4:15 PM CP09.02.07
Flow Instability Mechanism for Formation of Self-Ordered Porous Anodic Oxide Films Pratyush Mishra and Kurt R. Hebert; Department of Chemical and Biological Engineering, Iowa State University, Ames, Iowa, United States.

Electrochemical oxidation of aluminum in electrolytes that dissolve the oxide produces porous anodic oxides (PAO). For specific ranges of anodic voltages and electrolytes, highly ordered hexagonally arranged pores are formed with a well-defined scaling relationship between the spacing of nanoscale pores and the anodizing voltage. Nano PAO has been used for a wide range of applications, including dye-sensitized solar cells, biosensors, and templates for secondary nanomaterials such as carbon, polymers and semiconductor materials. Despite the diverse applications, the mechanism for self-ordering is not yet clearly understood. Recent studies have demonstrated the importance of oxide flow and mechanical stress generation during PAO formation. Here a mathematical model is developed that includes oxide flow as an essential mechanism that drives porous growth, combined with ionic migration and electrochemical reactions in the oxide. The oxide flow is driven by mechanical stresses at oxide film interfaces, volume expansion associated with electrochemical reactions and transport of species, and divergence of ionic migration flux in the oxide. A morphological stability analysis is performed at the inception of instability that leads to the formation of steady-state porous film. Shape evolution at both metal and solution interfaces is included, in contrast to our prior model in which the metal interface was fixed. Instability at the solution interface is determined by the competitive effects of destabilizing surface stress driven oxide flow and stabilizing oxygen ionic migration flux. Metal interface evolution results in a new instability mode due to pressure-driven flow driven by the surface stress at the solution interface. As a result, the present model predicts voltage-dependent pore spacing in good agreement with experimentally observed value. The model determines the sensitivity of pattern formation to critical process parameters and predicts their range of values required for the self-organization of PAO.

4:30 PM CP09.02.08
A Fully Coupled Diffusion-Mechanical Finite Element Modeling for Tin Dioxide-Coated Copper Anode System in Lithium-Ion Batteries Kyung Jae Jeong1, Hoon-Hwee Cho2 and Haeung Nam Han1; 1 Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); 2 Materials Science and Engineering, Hanyang National University, Daejon, Korea (the Republic of).

As the demand for lithium-ion batteries (LIBs) with high energy density, faster charging times and longer lifetimes has been increasing explosively, it has become very important to understand the huge volume change phenomenon during lithium-ion insertion and extraction in electrodes since those can affect mechanical stability in LIBs. Several finite element (FE) simulation models have been developed to investigate the diffusion of lithium-ion and the corresponding mechanical behavior in anode materials. However, all of the models share a common drawback in that they did not take the effect of hydrostatic stress into account caused by lithium-ion insertion. When a relatively high charging rate is required, it could be essential to consider the effect of hydrostatic pressure inside anodes in order to precisely describing the diffusion behavior of lithium-ion because the surface-locking problem occurs. In this study, we propose a fully coupled diffusion-stress FE model that simultaneously solves the diffusion process and stress equilibrium equations by taking into consideration the mechanical contact between the tin dioxide active layer and the copper foam, and the hydrostatic stress gradient inside the active layer as well as the complex geometric structures. The numerically calculated strain values are compared with the experimental strain data collected in operando using X-ray diffraction. The computed strain histories are in good agreement with the measured data, enabling the possibility of precisely predicting the mechanical behavior and performance of anode materials in LIBs by only using numerical FE modeling.

SESSIO10 CP09.03: Evolution of Interfaces and Grain Growth

Session Chair: Patricia Bauman and Dmitry Golovaty

Wednesday Morning, April 24, 2019
PCC West, 100 Level, Room 106 B

8:30 AM CP09.03.01

Phase field modeling is a powerful and versatile method used for the study of microstructure evolution, as it allows the prediction of arbitrarily complex microstructures of multi-
phase systems using continuous variables such as the solute concentration, and the order parameters, which act as phase identifiers. In order to compare the phase field predictions to experimental observations, recent work has focused on developing quantitative models that accurately describe the chemical and elastic properties of the systems of interest. However, quantitatively describing the kinetic properties of a system in a phase field model is not straightforward. Although the diffusion coefficient D of the solute might be known experimentally, the mobility L of the order parameters cannot be directly measured. As a result, L is often arbitrarily fixed to describe either a diffusion-controlled process or a reaction-controlled process. In this study, a method is developed to determine the value of the kinetic parameter L based on a comparison between experimental observations and simulation results. This method is applied to the study of zirconium hydride precipitation.

8:45 AM CP09.03.02 Multi-Phase Field Model of Localized Corrosion Kinetics with Corrosion Products Formation Talha Q. Ansari and San-Qiang Shi; The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Localized corrosion is one of the complex forms of corrosion which makes it difficult to detect and design-against. During metal corrosion in the corrosive environment, corrosion products are also formed as a result of electrochemical reactions inside the electrolyte. These products can precipitate on the corroding surface and stop/ slowdown the overall corrosion process. In order to understand this complex phenomenon, a multi-phase field model is proposed to simulate metal corrosion with corrosion products formation. Both anodic (metal oxidation) and cathodic (oxygen reduction) reactions along with other electrochemical reactions in the electrolyte are considered. The free energy of the system is described in terms of its metal ion concentration and the order parameters. Rather than considering linear kinetics (Allen-Cahn equation), inspired from classical rate theory, non-linear kinetics (Butler-Volmer) is considered to describe the temporal evolution of order parameters. The time dependent evolution of ionic species is governed by Nernst-Plank equations while electrostatic potential is governed by Poisson equation. The model results are compared with experimental findings and several examples are presented to show the practical applications of this model. One interesting example, which can be studied in detail with this methodology, is the formation of metal oxide nanowires (zinc/ aluminum oxide).

9:00 AM CP09.03.03 Precipitation and Strengthening Modeling for Disk-Shaped Particles in Aluminum Alloys—Size Distribution Considered Yue Li1,2,3, Hongxiang Li2 and Qiang Du2; 1University of Science and Technology Beijing, Beijing, China; 2SINTEF, Oslo, Norway; 3Norwegian University of Science and Technology, Trondheim, Norway.

For an ICME (Integrated Computational Material Engineering) modeling framework to be used for the age-hardening aluminum alloy design and heat treatment parameters optimization, it is critical to take into account the geometric shape of precipitates, as it is tightly related to the precipitation kinetics and particles’ hardening effect. The aim of this study is to present such an ICME modeling approach to describe the precipitation of disk-shaped hardening particles during aging treatment and predict the final yield strength. The classical Kampmann-Wagner Numerical (KWN) model is extended to consider the influence of disk-shaped particle morphology on growth kinetics. The extension consists of two correction factors to the growth rate equation and to the Gibbs-Thomson effect. The extended model, coupled with a metastable thermodynamic database, is applied to simulate precipitation kinetics of Al-Cu and Al-Mg-Zn alloys during aging treatment. The predicted microstructural features are in reasonable agreement with the reported experimental observations. Furthermore, a strengthening model for disk-shaped particles, which considers the size distributions of precipitates, is developed. The predicted yield strengths are compared with reported tensile test results and with predictions from other strength models. Unlike other models, the proposed strength model can reveal the strength contribution from disk-shaped precipitates without an additional tuning parameter for accounting for the impact of the mean particle spacing in the slip plane.

9:15 AM CP09.03.04 Refraction with Phase Discontinuities on Nonflat Metasurfaces Eric Stachura1, Cristian Gutierrez2 and Luca Pallucchini2; 1Kennesaw State University, Marietta, Georgia, United States; 2Mathematics, Temple University, Philadelphia, Pennsylvania, United States.

We provide a mathematical approach to study metasurfaces in nonflat geometries. Analytical conditions between the curvature of the surface and the set of refracted directions are introduced to guarantee the existence of phase discontinuities. Both the far field and near field cases are considered. The starting point is a vector form of Snell’s law in the presence of discontinuities on interfaces.

Our results are new since metasurfaces considered in the literature are normally flat, and the incoming radiation is directly normal to the surface. Our analysis allows for the possibility of designing non-flat metasurfaces for optical applications. In particular, we allow for a variable set of directions in which we want to refract radiation. There is a compatibility condition between the variable field and the surface that must be satisfied; in the case that the field is constant, this condition is trivially satisfied.

Our general analysis includes planar and spherical lenses as special cases, and we recover previous work of F. Capasso et. al. when the surface is a plane or a sphere, as one would expect.

This is joint work with C. E. Gutierrez and L. Pallucchini (Temple University).

9:30 AM *CP09.03.05 On the Voronoi Implicit Interface Method Alexander Zaitzeff, Selim Esedoglu and Krishna Garikipati; University of Michigan, Ann Arbor, Michigan, United States.

We present careful numerical convergence studies, using parameterized curves to reach very high resolutions in two dimensions, of a level set method for multiphase curvature motion known as the Voronoi implicit interface method. Our tests demonstrate that in the unequal, additive surface tension case, the Voronoi implicit interface method does not converge to the desired limit. We then present a variant that maintains the spirit of the original algorithm, and appears to fix the non-convergence.

10:00 AM BREAK

10:30 AM *CP09.03.06 Theory and Modeling of Abnormal Grain Growth Elizabeth A. Holm1 and Carl E. Krill2; 1Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Ulm University, Ulm, Germany.

Abnormal grain growth (AGG) occurs when an individual grain grows faster than the mean growth rate, and so achieves a size advantage that increases with time. AGG occurs in a wide variety of polycrystalline systems, including superalloys, nanocrystalline metals, and functional ceramics, and it can be desirable or detrimental. Despite its technological importance, the mechanisms and outcomes of AGG are not fully understood. In this presentation, we review AGG phenomenology and discuss the universal characteristics of AGG, namely the growth advantage and the persistence mechanism. Two approaches to modeling AGG are developed: A statistical model predicts the frequency of abnormal growth events as a function of microstructural characteristics and grain boundary properties, but does not capture the growth trajectories or morphologies of individual grains. In contrast, a local model based on grain boundary breakaway provides insight into the effects of grain characteristics and environment on the likelihood that a given grain will grow abnormally and on its outcome morphology. We will conclude by outlining the remaining knowledge gaps that may provide fruitful areas for further research.

11:00 AM *CP09.03.07 Shape and Composition Control in 2D-TMD Alloy Sheets—Benjamin "MoSe2" Franklin David J. Srolovitz1,2, Joel Berry1, Simeon Ristic2 and Songsong Zhou2; 1Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong; 2Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Hong Kong Institute for Advanced Study, City University of Hong Kong, Kowloon, Hong Kong.
Many transition metal (TM) dichalcogenide (TMD) trilayer sheets may be alloyed in the upper or lower chalcogen layers or within the TM layer. Since alloying elements typically are of different size than the atoms for which they substitute, alloying leads to localized strain which may cause bending in a free standing TMD sheet. On the other hand, bending the sheet creates spatially-localized site preference for the different alloying elements. This effect can be used to impart 3D sheet shapes through composition patterning or composition patterning through sheet bending. In this presentation we focus on shape and composition programming in MoSe$_2$S$_{0.5}$Te$_{0.5}$, i.e., MoSeS. We develop a compositional strategy to do this through a quantitative, first principles-informed continuum model for the coupled mechanics and alloy thermodynamics. We apply this method to optimizing the MoSeS composition profile to reproduce the topography of a Benjamin Franklin half-dollar coin. Non-uniform spatial composition distributions give rise to electric dipoles that may lie in-plane or perpendicular to the plane of the sheet (Janus structures). The shape of such compositionally-modulated Janus sheets may be dynamically actuated through application of an electric field.

11:30 AM CP09.03.08

Gamma-Convergence of Threshold Dynamics Algorithms

Tiago Salvador and Selim Esedoglu; University of Michigan, Ann Arbor, Michigan, United States.

I will report on recent developments in a class of algorithms, known as threshold dynamics, for computing the motion of interfaces by mean curvature. These algorithms try to generate the desired interfacial motion by alternating two very simple operations: convolution, and thresholding. I will present a simplified version of the threshold dynamics algorithm given in the work of Esedoglu and Otto (2015) for the isotropic multiphase case that does not require the use of retardation functions. I will discuss the stability and convergence of the proposed algorithm, and threshold dynamics in general, which rely heavily on the positivity of the convolution kernel and its Fourier transform. Some counterexamples in which Γ-convergence fails in the very simple isotropic, multiphase case will also be presented. Finally, I will discuss recent results on Γ-convergence of the two phase, anisotropic case for sign changing kernels. Our contribution, which will also be discussed, is enlarging the class of admissible sign changing kernels since it is possible to construct interesting anisotropies not covered by the previous work. Joint work with Selim Esedoglu.

11:45 AM CP09.03.09

Mathematical Modelling Beyond Computation—An Example on Epitaxial Growth of Magnetic Films for Tailoring of Magnetic Anisotropy

Artur Braun; Empa, Duesseldorf, Switzerland.

Epitaxial growth of metal films is an established and mature technology. The management of epitaxial strain is not a technical burden and difficulty, but opens new opportunities and functionalities in heterostructure materials. I am presenting here a case where epitaxial strain is exploited for the manipulation of the magnetic anisotropy, for example for applications in magnetic data storage. The materials engineer has only a limited set of materials and process parameters available, all of which shall be entered in an analytical mathematical model. In particular are these the elasticity of substrate including its lattice constant, and the magnetic parameters of the evaporation material including its lattice constant, plus the final film thickness. From these choices the elastic constants of the film material are immediately derived by standard materials databases. Now, an energy balance approach is used to enter the mathematical modelling. The result is a closed mathematical expression for the thickness (critical reorientation thickness) for the epitaxial film beyond which the magnetization axis switches into the film plane. The approach requires virtually no computing power. The model is tested for three different materials systems and delivers good match.


hydrodynamics interactions enhance MIPS. The transition to a phase-separated state strongly depends on the nature of the swimmer’s flow field, with an increased tendency toward MIPS for pullers, a reduced tendency for pushers. Thus, hydrodynamic interactions show opposing effects on MIPS for spherical and elongated microswimmers, and details of the propulsion mechanism of biological microswimmers may be very important to determine their collective behavior.

Hydrodynamic interactions play a particular role in systems with a large number of internal degrees of freedom like in filamentous, polymer-like structures. As simulation and analytical studies show, activity leads to swelling of flexible polymers, shrinkage and reswelling of semiflexible polymers, and an enhanced dynamics [3]. In such systems, hydrodynamics enhances shrinkage, modifies swelling significantly, and changes the intramolecular dynamics. The shrinkage, even in the presence of excluded-volume interactions, results in an enhanced packing, which might be important for polymer organization in confinement.


4:30 PM CP09.04.06
First-Principles Calculation of Third-Order Elastic Constants via Numerical Differentiation of the Second Piola-Kirchhoff Stress Tensor
Angelo Bongiorno; College of Staten Island - CUNY, Staten Island, New York, United States.

Third-order elastic constants allow to quantify and characterize the nonlinear elastic properties of a material, e.g. thermal expansion, Gruneman parameters, specific heats, sound wave mixing and attenuation, and elastic phase transitions. Measuring these physical parameters is difficult and prone to large errors, whereas current methods based on fitting energy-density curves, strain curves work well only for high symmetry crystals.

In this paper, we present and illustrate a novel method to calculate from first principles the full set of third-order elastic constants of a material of arbitrary symmetry. The method relies on a periodic first-principles scheme to calculate the Cauchy stress tensor of a material and numerical differentiation of the second Piola-Kirchhoff stress tensor to evaluate the elastic constants. Here we discuss an implementation of this method based on the use of a plane-wave density functional theory scheme to calculate the Cauchy stress tensor. In particular, we show that finite difference formulas lead to a cancellation of the finite basis set errors, whereas we propose simple solutions to eliminate the numerical errors arising from the use of Fourier interpolation techniques. Then, we show applications of our method to diamond, silicon, aluminium, magnesium, graphene, and a graphite conformer. In all cases, our method is shown to give results in excellent agreement with both the experiments and previous calculations based on fitting energy-density curves, thereby demonstrating both accuracy, validity, and generality of our new computational approach to investigate nonlinear elastic behaviors of materials.
Despite rapid penetration of computer technologies practically in any area of data analysis, manual peak labeling still remains the main technique for mass spectrum peaks identification procedure is crucial for accurate interpretation of the measured data [2, 3]. Of mass-spectrometry data [1] and requires preliminary establishing of correct correspondence between the peaks in the spectrum and the particular atomic species. This peak identification procedure is crucial for accurate interpretation of the measured data [2, 3].

Despite rapid penetration of computer technologies practically in any area of data analysis, manual peak labeling still remains the main technique for mass spectrum peaks identification. The procedure is time-consuming and vulnerable to errors [3]. Also, it is extremely difficult to take into account all the available information about the sample, the measured data and the possible correlations between detection of different ion species simultaneously during manual analysis.

Computer-assisted peak labeling has recently been shown to provide noticeable advantages over manual procedure [2]. However, large amount of work is still to be done in this area. First, it is desirable to have reliable physical and mathematical background, which the analysis algorithm could be based to at least its universality and the absence of adaptation to different measurement conditions. Also, the algorithm should be able to take into account all the information, known about the investigated sample a priori, which can be extremely useful for making the analysis result even better.

In this contribution, we propose a solution of the tasks listed above on the base of the Bayesian approach, which proved to be a powerful and useful tool for solving a very similar peak identification problem in powder X-ray diffraction [4]. The key idea of the proposed approach is to rank ions according to their probabilities, calculated from Bayes’ formula and conditioned by the measured data. More specifically, the initial information about the investigated specimen (e.g. presence or absence of some elements, correlations between certain ions’ detection, etc.) is encoded in prior probabilities of ions and their combinations. The expected inaccuracies of the measurement and peak search are quantified by the likelihood function. Based on the measured data, posterior probabilities are calculated for the specimen models (combinations of ions, possibly describing the actual measured data). The posterior probability for an ion is defined as the total probability of all the models, containing such ion, and can be estimated even without actual construction of all those models. If several ions have already been accepted as appropriate by the user, only the models containing those selected ions are taken into consideration. For each combination of ions, the corresponding optimal peak labeling is chosen by maximization of the measured mass spectrum likelihood.

The designed approach has been applied to a number of time-of-flight mass-spectrometry datasets, measured for inorganic samples (alloys and semiconductors). Each mass spectrum was iteratively analyzed by accepting one of the top-ranked ions at each step. A simple approach, when each ion is ranked according to the measured data and the already accepted ions only, was compared with “smart” peak labeling, when the higher probabilities of observing correlated ions groups (e.g. Te⁺ together with Te²⁺, Te³⁺ and TeO⁻) were taken into account. As one would expect, including the additional information into the analysis increased the quality of the obtained results and enabled reliable construction of sample models, consistent with the results of manual analysis.

In recent years, due to the energy crisis and environmental pollution, the researches on the issues of energy and environmental sustainability had attracted more and more attention. The clean renewable energy source, such as the solar power, provides the most promising way to face these challenges. In order to improve the efficiency of energy transfer, surface modification by wet chemical etching has become one of the most widely used approaches in this field. To control the surface and interface structures, the facets for forming the surface and interface are the key parameters that should be rationally selected. The facets exposed on the etched surface would affect the photovoltaic or photocatalytic performance through various working mechanisms. To understand and give insights into the growth mechanism of faceted morphologies by wet chemical etching, in this study a phase-field model was established to simulate the process of anisotropic chemical etching in a crystalline material. Different crystallographic materials, e.g. the cubic and hexagonal systems, were investigated. By altering the numerical parameters in the simulations, such as the etching rate, temperature, and the preferential etch orientation, the influences of the relevant experimental parameters on the formation and evolution of faceted morphologies were revealed. In addition, various featured surface morphologies, including the nano-pyramids and square columns, controlled by the anisotropy of the crystalline structures and etching rate were numerically reconstructed. These simulation results were consistent well with the observations of chemical etching experiments. This study was expected to offer fundamental knowledge and detailed information of surface modification by wet chemical etching for the advanced applications in solar energy technology.
The Peculiarities of Mathematical Modeling of Electromagnetic Stirring of Silicon Melt—A Crystallographic Model with the Emphasis on the Role of Partial Stacking Faults in HCP Metals

Lucy Johana Jiménez González

The research results are as follows:
- The requirements to the geometry and local specification of the triangulation computing mesh are determined.
- The approach based on the use of the Lorentz force averaging is justified for several periods.
- The possibility of calculating electromagnetic stirring under the conditions of nonsinusoidal current waveforms in inductors is provided.
- The possibility of calculating electromagnetic stirring within the conditions of inductors supply by voltage source is provided.
- The described approaches are illustrated by calculations of electromagnetic stirring for large volumes of silicon (65 crucible).

Recent studies have shown that graphene is one of the two-dimensional nanomaterials with vast applications due to its excellent structural, thermal, electrical, mechanical and magnetic properties, mainly in the field of biomedicine. Graphene doped with other materials and modified in its structure has achieved wide recognition among the academic and industrial sectors to create next-generation medical systems and therapies. In this work, we present novel stable molecular structures of modified graphene with doping or by changing the length of some of its bonds and obtaining physicochemical properties through multiscale methods including ab initio, quantum chemistry, force fields, mesoscopic methods, and statistical and thermodynamic methods. The results obtained in this work show that the, designed theoretically, modified graphene structures are suitable for the development of new devices for diagnostic, generation of bioimages in deep parts of the human organism, devices for targeted delivery of drugs and detection of macromolecules.

Computational Techniques for Calculating Material Properties from Coarse-Grained Epoxy Curing Simulations

Mike Henry, Stephen Thomas, Monat Alberts, Carla E. Estridge, Eric Jankowski, Micron School of Materials Science and Engineering, Boise State University, Boise, Idaho, United States; The University of Tennessee at Knoxville, Knoxville, Tennessee, United States; Next Generation Composite Materials, The Boeing Company, St. Louis, Missouri, United States.

The atomic displacement vectors associated with the zonal-twinning mechanism are derived analytically and expressed in a mathematical form generalized for the whole twinned domain of any HCP crystal with κ=c/a ratio within a practical range of 1.5<κ=c/a<1.9. This displacement field demonstrates that the atoms must move in a cooperative and coordinated manner during twinning.

For the special case of κ=3, a pure shuffling mechanism is predicted by the current model in which the shear type atomic displacement vectors are zero, and shear-shuffle type atomic displacement vectors become net shuffle type atomic displacement vectors without varying magnitudes with respect to the height of the twinned domain.

In contrast to the classical twinning mechanism, the new twinning mechanism suggests a simple and traceable pattern of atomic motions such that the associated absolute and relative magnitudes of the atomic displacement vectors are considerably smaller. Moreover, in the new mechanism, the resulted twinned lattice has a correct HCP structure, and the invariance of plain strain condition for (10-12) plane is preserved during twinning.

The new model describes a structural property of HCP metals, a new crystallographic model is developed for (10-12)<1011> twinning system.

Recent studies have shown that graphene is one of the two-dimensional nanomaterials with vast applications due to its excellent structural, thermal, electrical, mechanical and magnetic properties, mainly in the field of biomedicine. Graphene doped with other materials and modified in its structure has achieved wide recognition among the academic and industrial sectors to create next-generation medical systems and therapies. In this work, we present novel stable molecular structures of modified graphene with doping or by changing the length of some of its bonds and obtaining physicochemical properties through multiscale methods including ab initio, quantum chemistry, force fields, mesoscopic methods, and statistical and thermodynamic methods. The results obtained in this work show that the, designed theoretically, modified graphene structures are suitable for the development of new devices for diagnostic, generation of bioimages in deep parts of the human organism, devices for targeted delivery of drugs and detection of macromolecules.
Block copolyelectrolytes are one of the leading candidate materials for use as solid-state single-ion electrolytes (for ion transport) and ion-conductive membranes (for ion exchanging) in electrochemical energy storage systems, such as Li-ion batteries and fuel cells. They self-assemble into nanostructures that enable both ionic transport and maintain structural integrity. Ion transport in these charged block copolymers strongly depends on the alignment of specific anisotropic nanostructures. In this work, a modified dissipative particle dynamics (DDP) simulation framework has been developed to systematically study ion diffusion dynamics considering various experimentally controllable factors, such as block volume fraction, Flory-Huggins parameter, block charge fraction (or ion concentration), and dielectric constant. Using a novel “diffusivity tensor” approach, we predict the phase-dependent ion diffusivity along the principal micromdomain orientations, and find that the degree of anisotropy in ion diffusivity strongly correlates with that of the polymer microdomains. Ion conductivity in block copolyelectrolytes strongly depends on ion concentrations and temperatures, but weakly on other experimentally controllable parameters. Surprisingly, we discover that the inverse topology gyroid and cylindrical phases are the optimal candidates for single-ion conductors with high-flux ion conductivity, well-percolated isotropic diffusion pathways, and mechanical robustness. Finally, we find that higher ion diffusivity can be achieved by increasing the dielectric constant, which facilitates ion diffusion across block micromdomain interfaces. This work significantly motivates future efforts in exploring inverse phases without removing grain boundaries in order to enhance ion transport.

CP09.05.10 Computational Modeling of Surface Sputtering and Redeposition from Micro-Architected Surfaces Andrew Alvarado1, Hsing-Yin Chang1 and Jaime Marian1,2 1Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California, United States; 2Mechanical & Aerospace Engineering, University of California, Los Angeles, Los Angeles, California, United States.

As electronic propulsion continues to be a lucrative approach for space travel, the uncertainty of thruster and spacecraft component lifetimes solicit a need for a reduction in harmful effects. The recent developments of micro-architected surfaces show that these surfaces can partially negate the effects of plasma-induced sputtering and erosion. Due to the recent developments, the sparse collection of sputter yield data on micro-architected surfaces and materials remain an inhibiting obstacle. Therefore, we develop a 3D computational model to simulate the surface morphology evolution of micro-architected tungsten (W) samples and its instantaneous sputtering (erosion) rate under xenon (Xe) plasma exposure. We quantify the dynamic evolution of micro features of surfaces with built-in architecture and the corresponding variation in the sputtering yield through a Monte Carlo based ray-tracing method and adaptive meshing techniques. From our simulation, the surface profiles show the deposition of sputtered atoms as a result of geometric re-trapping and re-growth of surface layers. We find that micro-architected W samples exposed to 300 eV Xe plasma result in sputtering yield reductions of over 50% of the corresponding value for flat samples, indicating a self-healing mechanism of micro-architected surfaces under plasma exposure. Our model provides a framework allowing rapid expansion of its capabilities, such that the problem of sputtering redeposition from complex surfaces can be easily separated into a “physics” part (in idealized scenarios) and a “geometry” part (discretized to take advantage of the physical calculations).

CP09.05.11 Computational Modeling of Secondary Electron Emission from Micro-Architected Surfaces Hsing-Yin Chang1, Andrew Alvarado1 and Jaime Marian1,2 1Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California, United States; 2Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Surface erosion and secondary electron emission (SEE) of the channel walls of Hall-effect thrusters for space propulsion have been identified as the most critical life-limiting factors. Recently, new wall concepts based on micro-architected surfaces have been proposed to mitigate surface erosion and SEE. The idea behind these designs is to take advantage of very-high surface-volume-to-radius ratios to reduce SEE and ion erosion by internal trapping and redeposition. This has resulted in renewed interest to study electron-electron processes in relevant thruster wall materials. In this work, we present calculations of SEE yields in micro-porous W and BN surfaces using discrete event simulations. First, we study SEE as a function of primary electron energies between 100 eV and 1 keV and incidence angles between 0 and 90 degrees. For this, we use Monte Carlo simulations of electron multi-scattering processes, tracking the trajectories of primary electrons as they move through the materials and accounting for elastic and inelastic energy losses, as well as plasmonic/polaronic interactions. The results are then used to present the source term in ray-tracing Monte Carlo simulations of arbitrary geometry surfaces. We find that SEE yields in the energy range expected in Hall thruster conditions, are reduced several fold when using the new surface designs compared to ideal flat surfaces. This points to the suitability of these micro-architected surface concepts to mitigate SEE-related issues in compact electric propulsion devices.

CP09.05.12 The Sensitivity of the Electron Transport Response within Zinc Oxide to Variations in the Crystal Temperature, the Doping Concentration, and the Non-Parabolicity Associated with the Lowest Energy Conduction Band Valley Poppy Siddiqua1, Walid A. Hadi1, Michael Shur1 and Stephen K. O'Leary1 1School of Engineering, University of British Columbia, Kelowna, British Columbia, Canada; 2Department of Electrical, Computer, and Systems Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; 3Florida State University, Panama City, Florida, United States.

We examine how the character of the electron transport that occurs within zinc oxide is shaped by the crystal temperature, the doping concentration, and the non-parabolicity associated with the lowest energy conduction band valley. The aim of this analysis is to provide the emerging community of zinc oxide based device engineers with a detailed understanding of how the electron transport varies in response to changes in these parameters. While variations in the crystal temperature and doping concentration naturally arise from the range of device applications expected for zinc oxide based devices, the non-parabolicity coefficient associated with the lowest energy valley of the conduction band may be adjusted through the application of stress. An analysis of this effect will be presented. Both steady-state and transient electron transport responses will be considered within the scope of this analysis. The device implications of these results will be probed.

CP09.05.13 Simple Models for Testing Self-Assembly Robustness Rachel Singleton, Alex Chaney, Mike Henry and Eric Jankowski; Boise State University, Boise, Idaho, United States.

The robust self-assembly of proteins into virus capsids provides inspiration for designing synthetic building blocks that could aggregate into arbitrary structures, but the timescales of capsid assembly make atomistic modeling of such processes difficult. In this work we develop a simple simulation testbed for evaluating the assembly robustness of simple protein analogues and work towards modeling the conformational state changes that occur in real capsid proteins. We demonstrate how simple building blocks are difficult to design for robust assembly, and strategies for encoding desired structures into the design of individual particles. Finally, we discuss how such modeling techniques provide an accessible on-ramp for learning molecular simulations and intuitions for thermodynamic self-assembly.

CP09.05.14 Dislocation Dynamics of Deformation and Creep in Alloys Apay Annamareddy and Jacob Eapen; North Carolina State University, Raleigh, North Carolina, United States.

Alloy 709, which is an austenitic stainless steel strengthened with niobium, portrays excellent high temperature thermo-mechanical properties; it is currently being considered as a candidate material for the fast nuclear reactor program. Alloy 709 derives its high temperature strength from different precipitates such as M23C6 and M6C that are mostly formed at the grain boundaries, and nano-sized Z phase precipitates. These precipitates provide resistance to dislocation and grain boundary movements, and also improve resistance to creep. In this work, we use mesoscale discrete dislocation dynamics (DDD) simulations to investigate the mechanical deformation and creep behavior of model high temperature alloys under accelerated test conditions. In particular, we probe the dynamic interactions between the dislocations and the precipitates. At lower precipitate strengths, we show that the dislocations shear across the precipitates, but for higher strengths, the dislocations bypass by looping around the precipitates. As expected, the yield stress increases with increasing concentration of the precipitates. Further, the material also hardens with increasing strength of the precipitates, with the maximum hardening exhibited for Orowan strengthening. We also delineate the fundamental deformation mechanisms during creep and elucidate the correlations associated with the evolution of dislocations and interactions with the precipitates, at different stresses and temperatures.

CP09.05.15
Study of the Critical Probability of Percolation in a 3D Simulation System with Random Radius in Its Pores for Grids of Variable Size 

Gustavo M. Ángel, Yessica Yazmin C. Calderon-Segura and Genndady Burlak, Institute of Research in Basic and Applied Sciences, Cuernavaca, Mexico.

We study the filtration simulation in 3D porous materials, assigning pores with sizes in a solid medium represented by a 3D grid of variable size. We identify the clusters for each grid as well as the infinite cluster that determines its critical probability through the neighbor hybrid structure method, and we determine the depth of each cluster in the material as well as the volume of the infinite cluster that allows the filtration step in the materials. In this work several tests were performed varying the size of the grid that allows us to determine the importance of the size and how it affects the filtration in the simulated grids.

CP09.05.16

Predicting Assemblies of Complex Macromolecules for Organic Photovoltaics 

Mia Klopfenstein, Mike Henry, Evan Miller, Matthew L. Jones and Eric Jankowski; Materials Science and Engineering, Boise State University, Boise, Idaho, United States.

Understanding the packing of the molecules used in organic photovoltaics (OPVs) is necessary for predicting charge transport and understanding structure-property relationships of these devices. In this work, we perform molecular dynamics simulations to understand how complex macromolecules ranging from representative asphaltenes, to new electron acceptors like ITIC aggregate. We develop computational tools for initializing simulations of these molecules in isolation, as mixtures, and with polydispersity in molecular weight when appropriate. We find that pi-stacking drives the aggregation of molecules, including the formation of symmetrical stacks for planar molecules with few side-chains. Such structures are beneficial for charge mobility, a good thing for efficient organic solar cells. This work demonstrates the potential to use the oil refining waste (asphaltenes) as an ingredient for solar energy production and has potential for identifying molecular features that correlate with robust assembly for charge mobility.

CP09.05.17

Coupled Ray Tracing and Lattice Boltzmann Model of TiO\textsubscript{2} Micropillars Array for Water Purification 

Pegah Mir Abedini\textsuperscript{1}, Agnieszka Truskowska\textsuperscript{2}, Duncan Z. Ashby\textsuperscript{3}, Masaru Rao\textsuperscript{1} and Alex Greeney\textsuperscript{1, 2}; \textsuperscript{1}Material Science and Engineering program, University of California, Riverside, Riverside, California, United States; \textsuperscript{2}School of Mechanical, Industrial and Manufacturing Engineering, Oregon State University, Corvallis, Oregon, United States; \textsuperscript{3}Department of Mechanical Engineering, University of California, Riverside, Riverside, California, United States.

TiO\textsubscript{2} has been widely studied as a photocatalytic material due to its non-toxicity, chemical inertness, and high photocatalytic activity. Here, we explore the operational behavior of a novel TiO\textsubscript{2} micropillar array for treating recycled wastewater in space. A ray tracing model is used to model light adsorption, and the lattice Boltzmann method is used to simulate the water flow through the pillars and the evolution of hydroxyl radicals in the vicinity of the pillars.

CP09.05.18

Is Atomic Size-Mismatch a Sufficient Condition to Yield Fragility in Bulk Metallic Glass Forming Liquids? 

Tina Mirzaei; University of California, Riverside, Riverside, California, United States.

The fragility of glass forming alloys in their molten state is found to correlate with the alloys’ ductility as a glass. Fragility is the deviation of the temperature dependence of a liquid’s viscosity from Arrhenius behavior. It was recently shown that there are qualitative differences in the way the medium range order changes with temperature in strong vs fragile glass forming liquids. The relatively long range differences in atomic order hint at differences in cooperative packing of atoms in strong vs fragile alloys, and lead us to ask the question: is atomic size mismatch sufficient to cause fragility? The answer to this question made classical molecular dynamics models to be created for alloys of size mismatched, but chemically identical atoms. Simulations of these systems were performed across a range of temperatures and the viscosity and medium range order computed as a function of temperature.

Acknowledgments: The authors gratefully acknowledge the use of the National Science Foundation’s Extreme Science and Engineering Discovery Environment (XSEDE).

CP09.05.19

A Neural Networks Approach to Predicting the Orientations of Images 

Vincent Davis\textsuperscript{1}; \textsuperscript{1}Mathematics, North Carolina Central University, Durham, North Carolina, United States; \textsuperscript{2}North Carolina State University, Raleigh, North Carolina, United States.

Electron backscatter diffraction (EBSD) is a technique that describes the orientation of crystals in a sample. A series of deep convolutional neural networks was built to determine the orientation of a polycrystalline sample based on its electron diffraction patterns. By establishing a fixed coordinate system, a mathematical model will take .jpg files of a series of rotations as training data at a rate of approximately 250 seconds on each epoch. The networks determine the orientation of a sample image at substantially higher orders than traditional physics-based forward models. Statistical techniques are applied within the model to attain a loss in accuracy of only 5-8 degrees for rotations between 0 and 360 degrees. This simple and robust python software tool can be utilized in further offline analysis to index electron diffraction patterns much more efficiently while maintaining an average level of accuracy greater than or equal to 80%.

CP09.05.20

Surface Coupling Suppression by Nanostructure Manipulation in a SiO\textsubscript{2} Thin Film 

Sunny Sinu\textsuperscript{1}, Kartik Venkatraman\textsuperscript{1}, Peter Rez\textsuperscript{2} and Peter Crozier\textsuperscript{3}; \textsuperscript{1}School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; \textsuperscript{2}Department of Physics, Arizona State University, Tempe, Arizona, United States.

Electron energy loss spectroscopy (EELS) is an experimental technique providing structural and chemical information about a material. Recent advances in transmission electron microscopy (TEM) technology have improved the energy resolution of the electron beam which has realized the investigation of vibrational modes within a material [1]. When coupled with the exceptional spatial resolution of approximately 1 angstrom achievable with current aberration-corrected transmission electron microscopes, high resolution EELS mapping of the atomic structure, chemical and electronic properties, and now vibrational modes is possible. In the vibrational regime of EELS, electrons can excite vibrational coupled with the exceptional spatial resolution of approximately 1 angstrom achievable with current aberration-corrected transmission electron microscopes, high resolution EELS mapping of the atomic structure, chemical and electronic properties, and now vibrational modes is possible. In the vibrational regime of EELS, electrons can excite vibrational modes within the sample through short-range “impact” scattering and “long-range” dipole scattering. We focus on vibrational modes dominantly excited by dipole scattering. In polar dielectric materials like SiO\textsubscript{2}, as the electron beam is incident on the material, surface phonon polariton (SPhP) signals couple strongly at thicknesses employed in typical TEM sample geometries [2]. These surface coupling effects manifest as a peak signal in the “reststrahlen” band with thickness-dependent energy losses in the EELS spectra. In a SiO\textsubscript{2} truncated slab geometry, as the electron beam is incident on the SiO\textsubscript{2}/vacuum interface, there is a suppression in the intensity of the SPhP that is accompanied by an increase in the intensity of the SiO\textsubscript{2}/vacuum interface phonon polariton [3]. Our work aims to suppress the SPhP signal through manipulation of material nanostructure. Utilizing classical dielectric theory, we can simulate dipole scattering in TEM samples of SiO\textsubscript{2} [2]. Commercial software COMSOL Multiphysics can accurately simulate dipole scattering through finite element method while also considering phonon-polariton interactions. Through finite element method, we can calculate the electron energy loss probability when an electron beam transmits the material, which is corroborated with experimental spectra. We can now vary the nanostructure and compute the corresponding electron energy-loss probability for a given model geometry with ease. Current calculations show significant surface coupling suppression using a 2x2 array of nanoholes surrounding the electron beam. We believe this phenomenon is the result of increased SiO\textsubscript{2}/vacuum interface vibrational signal coupling, which will invariably reduce surface coupling intensity via surface peak reduction from competing vibrational modes. In practice, such nanoscale holes would be easily fabricated with conventional focused ion beam (FIB) lithography.

References:

[4] The support from National Science Foundation CHE-1508667 and the use of (S)TEM at John M. Cowley Center at Arizona State University is gratefully acknowledged.
Proton-conducting ceramic fuel cells (PCFCs) have been actively studied as a next generation alternative power source, thanks to their low operation temperatures (~800 K) [1]. BaZr1-xY2O3 (BZYO) and BaCe1-xY2O3 (BCYO) perovskites have been the two mostly studied electrolyte materials. Recently, BaZr1-xCe1-yO2 was introduced by mixing the two materials to overcome the weak points of the two materials; high sintering temperature and low grain-boundary conductivity in BZYO, and poor chemical stability in BCYO [2]. In this study, we used lattice statics and genetic algorithm [3] to find energetically stable lattice structures among many possible structures in BaZr1-xCe1-yO2 (y=0.15) bulk as a function of Ce content. The lattice volume increases with the Ce content, because Ce atom is bigger than Zr atom. Despite the increase in volume, the distance among Y atoms diminishes, indicating that the Y atoms are agglomerated with the Ce content. This behavior could be further explained by the interaction between Y atoms and oxygen vacancies. We also applied this procedure to study grain-boundary structures (sigma 3 and 5) [4].

References
The dynamic fracture of brittle solids is a particularly interesting collective interaction connecting both large and small length scales. Apply enough stress or strain to a sample of brittle material and one eventually snaps bonds at the atomic scale leading to fracture of the macroscopic specimen. We discuss a nonlocal model for calculating dynamic fracture. The force interaction is derived from a double well strain energy density function, resulting in a non-monotonic material model. The material properties change in response to evolving internal forces eliminating the need for a separate phase field to model the fracture set. The model can be viewed as a regularized fracture model. In the limit of zero nonlocal interaction, the model recovers a sharp interface evolution characterized by the classic Griffith free energy of brittle fracture with elastic deformation satisfying the linear elastic wave equation off the crack set. We conclude with a numerical analysis of the model which is joint work with Prashant Jha.

11:00 AM *CP09.06.06
Debonding of a Gel from a Rigid Substrate
devan hemao1, maria-carme calderer2, carlos garavito-garzon2 and suping lyu3; 1facultad de matematicas, pontificia universidad catolica de chile, santiago, chile; 2school of mathematics, university of minnesota, minneapolis, minnesota, united states; 3medtronic inc., plymouth, massachusetts, united states.

A variational model for the delamination of polymer gel thin films from rigid substrates is presented. A formal asymptotic analysis of a simplified 2D version of the underlying governing equations show that, as the film grows thinner, the absorption of the moisture of its surroundings tends to produce a homogeneous vertical stretch in the part of the film that remains bonded to the substrate and a state of free swelling in the debonded part. A transition layer, with a width comparable to the film thickness, is developed in order to connect the two swelling modes. This work is joint with carme calderer (u. minnesota), carlos garavito-garzon (u. minnesota) and suping lyu (medtronic inc.).

11:30 AM CP09.06.07
A Geometric Theory of Wrinkling for Confined Elastic Shells
ian tobacco; mathematics, university of michigan, ann arbor, michigan, united states.

Thin elastic membranes readily take on shapes wildly different from their own. Motivated by recent experiments on wrinkling patterns observed in thin floating shells, we obtain a fully rigorous asymptotic expansion of the energy (elastic and otherwise) valid in the highly-wrinkled limit. After renormalizing by the typical energy of wrinkling, we derive a coarse-grained model in which an elastically compatible pattern is assigned energy proportional to the difference between its intrinsic undeformed area and its projected area in the plane. Energetically optimal patterns therefore maximize their projected area. Surprisingly, this limiting model turns out to be explicitly solvable in a large variety of cases, including for shells whose (possibly non-constant) curvature is of a known sign. We demonstrate our methods with concrete examples and offer comparisons with experiments. What results is an ansatz-free explanation for the geometry of wrinkle patterns seen in confined thin elastic shells.

11:45 AM CP09.06.08
Asymptotic Analysis of the Helical Twisting Power of Chirally Doped Nematics
jamie m. taylor;bcam, bilbao, spain.

Elongated molecules with mirror symmetry have a tendency to form nematic phases, where the ground state is constant in space and molecules roughly point in the same direction. However, the introduction of a small quantity of chiral molecules can be enough to cause a helically twisted ground state, with periodicity comparable to the wavelength visible light, making them ideal for many applications related to optics. The Helical Twisting Power (HTP) is the constant of proportionality between the concentration of dopant and the frequency of the ground state in dilute systems, and quantifies the ability of the dopant to twist the host ground state. Typically HTP depends highly on both the dopant and host, and may increase or decrease with temperature. In this work we attempt to understand the HTP by considering a mean-field model, which is essentially a non-local Landau-de Gennes type model describing coupling between the dopant and host species, accounting for the symmetries of their long-range attractive pairwise interactions. The model contains many terms and is illusive, but by taking a simultaneous large domain and dilute dopant limit in a periodic domain, we can obtain the Oseen-Frank free energy for cholesteric liquid crystals, and can relate the macroscopic HTP with certain scalar quantities derived from the pairwise molecular interactions. In particular, we see that in essence the HTP is heavily related to the ratio of quantities relating to the strength of achiral Host-Host interaction and chiral Host-Dopant interaction, and the qualitative temperature dependence of HTP changes depending on their relative strength.

SESSION CP09.07: Mathematics of Nanoscale Structures and 2D Materials
Session Chairs: Patricia Bauman, Maria Emelianenko and Dmitry Golovaty
Thursday Afternoon, April 25, 2019
PCC West, 100 Level, Room 106 B

1:30 PM *CP09.07.01
Plasmonics on 2D Materials—A Flavor of Dispersion and Homogenization
Dionisios Margetis; Mathematics and IPST and CSCAMM, University of Maryland, College Park, Maryland, United States.

In the last decade, tremendous advances have been made in the design and fabrication of 2D materials with novel electronic structures. Celebrated examples of such materials include graphene, black phosphorus and van der Waals heterostructure. The surface conductivity in the infrared regime in some of these systems may allow for the propagation of fine-scale electromagnetic waves, called surface plasmon-polaritons (SPPs), which can defy the usual diffraction limit. In this talk, I will discuss macroscopic consequences of the optical conductivity of 2D materials via solutions of classical Maxwell's equations. In particular, I will formally discuss how geometry, i.e., the presence of material edges and curvature, can influence SPP dispersion. In addition, I will show how slowly varying waves with nearly no phase delay may possibly propagate through suitably designed plasmonic crystals.

2:00 PM *CP09.07.02
Multiscale Modeling of van der Waals 2D Stacked Materials
john lowengrub1; zhenglu guo1 and vivek b. shenoy2; 1mathematics and chemical engineering & materials science, university of california, irvine, irvine, california, united states; 2materials science, university of pennsylvania, philadelphia, pennsylvania, united states.

Vertical stacking of monolayers via van der Waals (vdW) interaction opens promising routes toward engineering physical properties of two-dimensional (2D) materials and designing atomically thin devices. However, due to the lack of mechanistic understanding, challenges remain in the controlled fabrication of these structures via scalable methods such as chemical vapor deposition (CVD) onto substrates. In this talk, we develop a general multiscale model to describe the size evolution of 2D layers and predict the necessary growth conditions for vertical (initial + subsequent layers) versus in-plane lateral (monolayer) growth. An analytic thermodynamic criterion is established for subsequent layer growth that depends on the sizes of both layers, the vdW interaction energies, and the edge energy of 2D layers. We then explore the effect of nonlinearity using a new, 2nd order accurate diffuse domain formulation of the governing equations that places no constraints on the morphologies of the islands. We find that the analytic criterion accurately captures the conditions for which the 2nd layer grows even when the morphologies are complex (e.g., highly anistropic, have negative curvature, etc.). Our model agrees with experimental observations of monolayer and bilayer growth of graphene and other 2D materials by CVD.

2:30 PM *CP09.07.03
Multiscale Modeling of Weakly Interacting Incommensurate 2D Lattices
j.p. wilber, dmitry golovaty and malena espanol; university of akron, akron, ohio, united states.

We derive a continuum variational model for a two-dimensional deformable lattice of atoms interacting with a two-dimensional rigid lattice. The starting point is a discrete atomistic model for the two lattices, which are assumed to have slightly different lattice parameters and, possibly, a small relative rotation. This is a prototypical example of a three-dimensional system consisting of a graphene sheet suspended over a substrate. A discrete-to-continuum procedure is used to obtain a continuum model that recovers both qualitatively and quantitatively the behavior observed in the corresponding discrete model. The continuum model predicts that the deformable lattice develops a network of domain walls characterized by large shearing, stretching, and bending deformation that accommodates the misalignment and/or mismatch between the deformable and rigid lattices. Two
integer-valued parameters, which can be identified with the components of a Burgers vector, describe the mismatch between the lattices and determine the geometry and the details of the deformation associated with the domain walls.

2:45 PM BREAK

3:15 PM CP09.07.04

Hamiltonians and Order Parameters for Crystals Containing Orientable Molecules John C. Thomas, Jonathon Bechtel and Anton Van Der Ven; University of California, Santa Barbara, Santa Barbara, California, United States.

Crystalline materials containing easily reorientable molecular species are an increasingly important category in the search for modern functional materials. Such materials include hybrid organic–inorganic halide perovskites, a record-breaking class of photovoltaic materials. Despite current interest in these materials, orientational fluctuations of arbitrary molecules are challenging to describe mathematically and do not fall within the conventional lattice models of solid state physics. The presence of orientable molecular species thus constitute a significant hurdle to truly predictive simulation of thermodynamic and kinetic phenomena in these promising materials.

In this talk, we present a mathematical framework for constructing accurate anharmonic model Hamiltonians that express the crystal potential energy in terms of collective orientations of interacting molecular ions, which we abstract as rigid rotors. The approach is motivated by the cluster expansion framework from alloy theory and is appropriate for describing both chiral and achiral molecules. By utilizing a quaternion parameterization of molecular orientation, along with a hyperspherical harmonic basis set, we are able to construct Hamiltonian expressions that reflect all symmetries of both the host crystal and the molecular species. The resulting Hamiltonian is compact, systematically improvable, and suitable for Monte Carlo or molecular dynamics simulation. Moreover, the basis functions employed in constructing the Hamiltonian are useful as order parameters for characterizing orientational order and phase transitions. We describe results obtained via this method for the CH₃NH₃PbX₃ lead-halide hybrid perovskites, including symmetry-adapted order parameters and Hamiltonian basis functions.

3:30 PM CP09.07.05

A Practical Approach to Bypassing Kohn-Sham DFT Using Machine Learning Techniques Amit Samanta and John Klepley; Lawrence Livermore National Laboratory, Livermore, California, United States.

The Kohn–Sham scheme of density functional theory (KS-DFT) is popularly used to solve electronic structure problems in materials for applications, like catalysis, hydrogen storage, electronic and optical applications, mechanical strength and phase stability. In this talk, I will present a machine learned DFT (ML-DFT) framework that can be used to predict the energy and forces for a given atomic structure at significantly reduced computational cost. This ML-DFT framework relies on two different machine learning models, one that allows us to predict the ground state charge density of a structure and another that allows us to predict the total energy and forces acting on each atom from the ground state charge density. We believe such a framework can be used to handle multi-component systems, systems that involve charge transfer during evolution and in principle can also be trained using a database derived from hybrid functional calculations. This ML-DFT framework requires fewer computing resources than direct KS-DFT calculations, meaning that a system can be evolved for longer durations using molecular dynamics with ML-DFT. In addition, the memory requirements in ML-DFT are limited to storing the charge densities of structures in the database. This fact suggests that system sizes (up to 4000 atoms) can be studied that are not easily accessible in KS-DFT.

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

3:45 PM CP09.07.06

Thermal/Electrostatic Green’s Function for 2D Phosphorene/Metal Composite and Possibility of Its Measurement by Using SPM Vinod K. Tewary and Edward J. Garboczi; National Institute of Standards and Technology, Boulder, Colorado, United States.

Mathematically modeling of materials is emerging as an independent branch of materials science. A mathematical model of a material plays a major role in the characterization and production of real materials as it provides a prototype for virtual experimentation. In this talk, I will present a machine learned DFT (ML-DFT) framework that can be used to predict the energy and forces for a given atomic structure at significantly reduced computational cost. This ML-DFT framework relies on two different machine learning models, one that allows us to predict the ground state charge density of a structure and another that allows us to predict the total energy and forces acting on each atom from the ground state charge density. We believe such a framework can be used to handle multi-component systems, systems that involve charge transfer during evolution and in principle can also be trained using a database derived from hybrid functional calculations. This ML-DFT framework requires fewer computing resources than direct KS-DFT calculations, meaning that a system can be evolved for longer durations using molecular dynamics with ML-DFT. In addition, the memory requirements in ML-DFT are limited to storing the charge densities of structures in the database. This fact suggests that system sizes (up to 4000 atoms) can be studied that are not easily accessible in KS-DFT.

The connection between the GF and the process of measurement arises from the fact that the GF corresponding to an operator is the inverse of that operator. In Physics, the process of measurement of a quantity for a system is represented by an operator equation, which gives the response of the system to an applied probe. The GF is independent of the probe. For example, if we have a system whose GF is known, we can calculate the response of the system to any probe.

On the experimental side, in a typical scanning probe microscopy (SPM) experiment, one measures the response of a sample to a point probe or a distribution of point probes. Interestingly, that is exactly the mathematical definition of the Green’s function – response of a material to a point probe. With the recent developments in the science and technology of SPM, it should be possible, at least in principle, to measure the GF of a material system for the SPM measurement. It would prove to be an especially useful technique for the new 2D semiconductors. In these systems, it is still a challenge to understand the relationship between their structure and their physical properties. Understanding such relationships is vital for their engineering industrial applications.

In this talk, I will describe a new and computationally powerful technique for calculating GFs for the Laplace/Poisson equation for the thermal/electrostatic response of a system of 2D composite materials. The technique is based on a partial Fourier representation of the GF. In this representation, integration over one variable can be obtained analytically, which results in a substantial economy of computational time and effort. We have used this technique for calculating the response map of anisotropic 2D phosphorene containing a metallic inclusion. Phosphorene and its composites are materials of strong topical interest because of their potential applications in electronic and other devices. We have also used our formulation to calculate an effective value of the conductivity of the composite, which can be a useful single parameter for preliminary design of devices. Numerical results will be presented and discussed.

4:00 PM CP09.07.07

Role of Mesoscopic Friction and Network Morphology in Carbon Nanotube Yarn Formation—A Distinct Element Method Study Yuezhou Wang, Hao Xu, John C. Thomas, Jonathon Bechtel and Anton Van Der Ven; University of California, Santa Barbara, Santa Barbara, California, United States.

Carbon nanotube (CNT) yarns are promising synthetic nanomaterials for a variety of applications. To better understand the mechanism for yarn formation process, we performed mesoscopic scale distinct element method (mDEM) simulations for the stretching of CNT networks. With parameters input from full atomistic simulations, mDEM bridges across the atomistic and mesoscopic length scales. Our model predicts accurately the mechanical response of the network over a large deformation range. At small and moderate deformations, the model predicts accurately the mechanical response of the network over a large deformation range. At small and moderate deformations, the model predicts accurately the mechanical response of the network over a large deformation range.
Assessing the Size Effect on Frank-Read Source Operation in f.c.c Metallic Materials Through Concurrent Atomicstic-Continuum Simulations

Cobalt-based superalloys with γ′ microstructures offer great promise as candidates for next-generation high-temperature alloys for applications in, e.g. turbine blades. It is essential to understand the thermodynamic and kinetic factors that influence the microstructural evolution of these alloys in order to optimize the alloy compositions and processing steps with a goal to improve their coarsening, creep and rafting behavior. We are developing a phase field approach to study the diffusion process and to predict the equilibrium shapes of Co-AEW γ′ precipitates. In order to obtain quantitatively predictive capabilities we use a combination of molecular dynamics simulations, 3D atom probe tomography, and thermodynamic data to obtain bulk and interfacial energies, misfit strain, elastic constants and mobilities. A particular focus of our study is to understand how different energy balances, misfit strain and kinetics affect the rafting behavior and necking of γ′ precipitates, building on a previous model [1]. Apart from the shape bifurcation behavior reported in the previous work, we observe other characteristic microstructures as a result of the competition between the bulk free energy, interfacial energy, and elastic energy. The results indicate that the form of the bulk free energy may also have an influence on the equilibrium shape of the γ′ precipitates. Bulk free energy properties such as the separation between free energy minima and the height of the barrier between them may indirectly affect the morphology of the precipitates, as the total interfacial free energy also depends on this barrier. We are examining how the form of the bulk free energy affects the coarsening and rafting behavior of superalloy models, especially when the composition changes across interfaces.


8:30 AM CP09.08.01 Acousto-Plasmonic Coupling—The Raman Energy Density (RED) Nicolas Largé, Joe Luís Montalvo-Prieto, Lucien Saviot and Adnen Mlayah; Department of Physics & Astronomy, The University of Texas at San Antonio, San Antonio, Texas, United States; Laboratoire Interdisciplinaire Carnot de Bourgogne CNRS, Université de Bourgogne, Dijon, France; Centre d’Elaboration de Matériaux et d’Etudes Structurales CNRS, Université de Toulouse, Toulouse, France.

Most of the studies done around the plasmonic properties of metallic nano-objects are based on static measurements. Nevertheless, nano-objects are continuously changing in size and shape driven by the vibrations of their lattice. Therefore, the plasmon properties of the nano-objects are being modulated by the lattice vibrations, and vice versa. We present the study of the interaction between the acoustic plasmonic properties of metallic nano-objects and the localized surface plasmon resonance (LSPR) which give rise to a low-frequency Raman scattering response. The resonant Raman scattering process is described using a new approach on a single acousto-plasmonic interaction step described by a Fermi golden rule. In this effort, we introduce the concept of Raman energy density (RED) which represents the electromagnetic energy density excited by the Raman probe and modulated by the acoustical vibrations of the nano-object. To illustrate this new concept, RED spatial distributions and the Raman spectra are calculated for a gold nanoparticle with 5 nm in radius excited at its LSPR which give a clear picture of the coupling between the plasmon and the first isotropic and anisotropic acoustic vibrations (breathing and quadrupolar modes) and these are in good agreement with the experimental reports.

8:45 AM CP09.08.02 Assessing the Size Effect on Frank-Read Source Operation in f.c.c Metallic Materials Through Concurrent Atomicistic-Continuum Simulations Thanh Phan, Rigelesaiyin Ji and Liming Xiong; Iowa State University, Ames, Iowa, United States.

The Frank-Read (FR) source is one of the main dislocation multiplication mechanisms in crystalline materials. A FR source can produce multiple dislocations which may pile up against a grain boundary or other material interfaces. In a typical polycrystalline engineering material, the diameter of a dislocation loop generated from a FR source may be hundreds of nanometers and even above, which is beyond the reach of traditional optical microscopy. Moreover, the artificial force from free surface or periodic image on FR source in an atomistic model is often significant due to its length-scale limit. In this work, we use a freely developed concurrent atomistic-continuum (CAC) computational tool, which is based on a theoretical framework that unifies the atomistic and continuum description of materials, we simulate growth of a micron-sized dislocation loop through a FR source from the bottom up. At a fraction of the cost of full MD, CAC overcomes the length-scale limitation of MD and scale up the model up to several microns and even above, in which the image force effect becomes negligible. It enables us to systematically calibrate the relationship between FR source length and the critical shear stress for dislocation bowing out from the atomistic to the micrometer level. This work demonstrates the applicability of CAC in predicting the dynamics of dislocations at the mesoscopic level. It also opens up the possibilities of understanding a variety of dislocation-interface reactions which require a fully atomistic resolution near an interface and a coarse-grained material description of the long-range interactions between dislocations away from the interfaces in materials.
Due to its outstanding electromechanical properties, lead titanate (PbTiO₃) and its solid solutions, such as Pb(Zr, Ti)O₃ (PZT) and Pb(Mg₁/₃, Nb₂/₃)O₃-PbTiO₃ (PMNPT), have been widely applied in technological devices like non-volatile random access memories (FeRAMs), micro-actuator and sensors. For such materials, a slight atomic displacement strongly affects both mechanical and ferroelectric (FE) properties. Thus, a proper understanding of the atomic behavior of ferroelectrics is required. Computational simulation is a promising tool for analysis of the properties above. In this study, we have successfully reparameterized the core-shell model to model PbTiO₃. The new parameters considered the crystal structures, elastic properties and phonon frequencies which calculated by ab-initio density functional theory calculations. In addition to material mechanical properties, it can reproduce the thermodynamic properties like isometric heat capacity, adiabatic compressibility. Moreover, the new parameters were also tested by molecular dynamics simulations to examine the predictive ability at finite temperature. The phase transition temperature of 490 °C from the tetragonal to the cubic phase was obtained, which is consistent with experimental results. Furthermore, the new model was then used to study the interfacial effect on ferroelectricity at the nanoscale. The observed morphology changes of the ferroelectric domains at various temperatures, with or without an electric field in bulk, thin film and nano-rods match with the experiments. From the simulated models, a deeper understanding of the domain motion in atomic scale was achieved.

**9:30 AM BREAK**

**10:00 AM CP09.08.05**

**Quantifying the Length-Dependent Mobility of Dislocations in Metallic Materials from the Atomsitic to the Microscale**

Riipelaavin Il, Thanh Phan and Liming Xiong; Iowa State University, Ames, Iowa, United States.

In this work, the mobility of dislocations in f.c.c. and b.c.c. metals under deformation is quantified using a recently developed coarse-grained (CG) atomistic model. Fundamental to the CG method is an atomistic field formulation that unifies the atomic and continuum description of materials through an Irving-Kirkwood procedure in statistical mechanics. At a fraction of the cost of full molecular dynamics (MD), the CG model is shown to be applicable for calibrating the dislocation mobility law from the bottom up. In particular, using a modest computational resource, the mobility of extremely long dislocation lines (a length up to one micron and even above) in billion-atom material samples under deformation is predicted from the atomistic to the microscale. Results show that the dislocation mobility law in f.c.c. materials is insensitive to its length. In contrast, in b.c.c. materials, when the length of a dislocation is at micron level and above, its mobility is found to be proportional to the line length, i.e., the longer the dislocation line, the faster it moves. With the atomistic information being retained, the CG simulations also provide an explanation for the observed different line length-dependent dislocation mobility in f.c.c. and that in b.c.c. materials: both short and long dislocation lines in f.c.c. materials migrate through gliding, while dislocation motion is mainly controlled by kink pair nucleation and diffusion in b.c.c. materials, and the length will be the limiting factor for kink pair density. In parallel, in order to validate the CG model, a limited set of full MD simulations has been also performed. The one-to-one comparison between CG and MD demonstrates that the CG simulation does retain the atomic nature of dislocation dynamics, such as (i) the dislocation velocity-dependent line energy and core structure; and (ii) the phonon wave emission from a moving dislocation. In addition, the limitation, the future development, and the potential applications of CG will be also discussed in this presentation.

**10:15 AM CP09.08.06**

**Determining the Optimal Phase-Change Material via High-Throughput Calculations**

Nicholas Pike¹ and Ole Martin Lovvik²-³; (University of Oslo, Oslo, Norway; SINTEF Industry, Oslo, Norway).

The discovery and optimization of phase-change materials is often a long and expensive process. Here we propose a simple computational method to determine the ideal phase change material for a given chemical composition. Using first-principles calculations, within a high-throughput computational framework, we are able to determine the ideal composition of a phase-change material between any two assumed phases. This ideal composition is determined by a calculation of the co-factor conditions which, when equal to 1, ensure the lowest possible interface energy during the phase change. This ideal composition can then be targeted to produced materials with low mechanical failure rates due to the low interface energy. Here we will provide evidence of the effectiveness of our calculations for two well-known phase change materials in which we predict the ideal composition and compare it to experimental results.

**10:30 AM CP09.08.07**

**Coarse-Grained Modeling for Polymer Solutions via the Mori-Zwanzig Formalism**

Shu Wang and Wenxiao Pan; Mechanical Engineering, University of Wisconsin–Madison, Madison, Wisconsin, United States.

In this talk, we present a new method to establish implicit-solvent coarse-grained (CG) modeling for polymer solutions to conserve the dynamical properties of polymers. In the CG modeling, tens to hundreds of atoms were grouped as one CG particle; and the CG dynamic equations were rigorously derived from the atomistic data. The solvent-mediated dynamics of polymers was accurately captured via the generalized Langevin equation (GLE) with a non-Markovian memory kernel based on the Mori-Zwanzig formalism. The computational cost for direct evaluation of the non-Markovian memory kernel and generation of colored noise was significantly reduced by exploiting the equivalence between the non-Markovian dynamics and Markovian dynamics in an expanded space. A higher-order time-integration scheme was developed to further accelerate the CG simulations. To assess, validate, and demonstrate the established CG modeling, we have applied it to simulate four different types of polymer solution systems. We find that the proposed CG modeling effectively conserves the velocity autocorrelation function and diffusivity of polymers and enables two orders of speedup in computer time, compared with the reference molecular dynamics simulations.

**10:45 AM CP09.08.08**

**Real-Space Formulation for Simulating Defects in Crystalline Materials from First Principles**

Swarnava Ghosh, Kaushik Bhattacharya and Michael Ortiz; California Institute of Technology (Caltech), Pasadena, California, United States.

Density Functional Theory (DFT) has the highest accuracy to cost ratio among all electronic structure methods and provides valuable insight in understanding and predicting a wide range of materials properties. Defects in crystalline solids, play crucial role in determining macroscopic properties of materials. The profound significance of defects underlies from the coupling between the discrete effects of the lattice; chemical effects of the core and the long-range effects of the elastic field. While DFT is capable of accurately describing the chemistry of the defect core, but are too complicated and expensive for defects with long range fields, methods capable for describing long-range fields rely on empiricism and lack fidelity. This poses an outstanding dual challenge to simulate defects from first principles. To overcome this, we develop a novel coarse-grained formulation of DFT. We employ Linear Scaling Spectral Quadrature method to solve for the electronic fields and develop a coarse-graining strategy based on updated Lagrangian method to describe the long-range elastic fields. We discuss a real space formulation based on high-order finite differences, local reformulation of electrostatics, reformulation of the atomic forces and a parallelization strategy based on domain decomposition method. The developed formulation is sublinear scaling with respect to the system size and can efficiently simulate defects in crystalline materials from first principles calculations.

To demonstrate our framework, we use magnesium, the lightest among all commonly used structural metals, and has a high strength to weight ratio, and therefore has the potential to be significantly integrated into a wide range of applications. Existing magnesium alloys show low spall strength, which inhibits their applicability in dynamic environments. Magnesium alloys achieve their desirable mechanical properties via age hardening, and controlling the size of precipitates is necessary for spall strength. We use first principles calculations to understand the energetics of precipitation in magnesium-aluminum binary alloys and report the influence of deformations (which arise during processing) on the energetics of the precipitation process. We show strong dependence of concentration and volumetric strains on the cohesive energies of binary solid solutions and report a power law for these mixtures. We also show that the formation enthalpies of the solid solutions are dependent on the concentration and hydrostatic stress. The free energies of the solid solutions reported in this study are used to draw insight into the precipitation process. Since vacancies serve as nucleation sites for voids, which lead to spall, we also discuss the interaction of point defects (vacancy-solute, solute-solute and vacancy-vacancy) in magnesium-aluminum alloys using first principles calculations.
In organic electronics, it is critically important to understand how chemical structure influences molecular packing, carrier transport, and ultimately device performance. The self-assembly properties of liquid crystalline semiconductors offer many interesting advantages for fabricating highly ordered molecular films with interesting properties, including high carrier mobilities and good thermal stability.

This tutorial will provide a comprehensive overview of molecular self-assembly and liquid crystallinity in organic electronics. We aim to highlight the great potential for exploiting these effects in large-scale applications. We will begin by introducing the basics of liquid crystalline small molecules and polymers, liquid crystalline mesophases, film processing and characterization, and device physics. Relevant experimental and theoretical tools for studying this class of materials will be introduced. Finally, we will survey state-of-the-art results on the application of liquid crystalline semiconductors in high performance organic electronics.

This tutorial is aimed at experimentalists and theorists in physics, chemistry, and material science.

1:30 PM
**Basics of Liquid-Crystalline Small-Molecule Semiconductors—Liquid Crystals as an Organic Semiconductor from Materials to Devices**
Jun-ichi Hanna; Tokyo Institute of Technology

The basics of liquid crystalline small molecule semiconductors, with focus on controlling molecular order via liquid crystalline mesophases, electrical transport in liquid crystalline films, device physics and applications.

2:30 PM BREAK

3:00 PM
**Liquid Crystallinity in Conjugated Polymers**
Enrique Gomez; The Pennsylvania State University

The basics of polymeric liquid crystalline semiconductors, with focus on molecular design, controlling molecular order, film characterization, electrical and optical properties.

4:00 PM
**Investigating Transport in Liquid Crystalline Semiconductors**
Elizabeth von Hauff; Vrije Universiteit Amsterdam

Concepts of carrier transport in organic semiconductors with focus on how molecular ordering determines transport phenomena.
The molecular structure of the backbone of semiconductor polymers determines the electronic levels that are relevant for organic electronic devices. Sidechains are added to the backbone to enable solution-processing by improving solubility. While the sidechains are relatively isolated from the electronic structure of the backbone, they play a significant role in the final morphology and molecular packing in thin films of semiconducting polymers. We have examined how sidechains control the resulting microstructure in thin films of a series of high performance co-polymers. Using a combination of high resolution transmission electron microscopy (HR-TEM) and grazing incidence wide angle X-ray scattering (GIWAXS) we have determined connections between sidechain structures and the domain boundaries in ordered donor-acceptor polymers. HR-TEM reveals that the aspect ratio of the crystallographic repeat unit of the backbone and sidechain length helps to determine the possible structure of domain boundaries. We have also studied conjugated polymers with unique macrocyclic sidechains that reveal the photophysical behavior of conjugated backbones without the interference of aggregation. These investigations reveal that sidechains should be considered from the outset of the design of new semiconducting polymers.

The presence of unknown polymorphs within thin films is a frequently observed phenomena for organic electronic molecules. These polymorphs can have considerably different optical and electronic properties which influences the device performance in organic electronics and optoelectronics considerably. A first step of understanding the origin of substrate induced phases is the determination of the molecular packing. A combination of grazing incidence x-ray diffraction with molecular dynamics simulation is used for crystal structure solution. Recently, also single crystal diffraction is used for crystal structure solution of substrate induced phases. We selected a number of different molecules and demonstrate fundamental properties of the crystalline structure in relation to the bulk crystal structure. It is shown that confirmation of the molecular packing with the substrate surface is an important parameter, additionally the different polymorphs can show fundamental different packing motifs like herringbone packing and stacking of aromatic rings. In a subsequent step the importance of the crystal growth kinetics is presented which causes the substrate induced polymorph and finally the thermodynamic stability of these phases. The selected examples are molecules which forms van der Waals crystals like pentacene [1], benzo[b]thiophene-benzothiophene based molecules [2] and oligothiophenes [3] but also examples from molecules with hydrogen bonds are discussed like dibromo-indigo [4] and dicyano-distyrylbenzene [5].

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Solution-processed organic thin-film transistors (OTFTs) have received enormous interest due to their great potential for realizing low-cost, lightweight and flexible electronics applications such as displays, wearable sensors and electronic skins. Although several novel solution-processing techniques for achieving highly-crystalline organic semiconductor (OSC) films have been introduced to OTFTs, there still remains a challenging work to control thin-film properties, such as crystallinity, morphology and uniformity accompanying the rapid coating speed demanded for industrial-scale production. Here, I will present a new solution coating method that is compatible with a fast-moving roll-to-roll system by using a gap-controlled wire-bar and a bar-motion programming strategy. The developed method is highly practical and industry-friendly as well as feasible to fabricate high-quality OSC thin films in a large area at a high rate. In this method, we found that blending of high-crystalline semiconductor small molecules and an amorphous semiconducting polymer additive in an active ink could significantly improve the crystallinity of the small molecular semiconductor layer with the aid of efficient vertical phase separation during the process. Using the motion programmed bar-coated blend OSC thin films, we demonstrated large-area flexible single-crystal OTFT arrays with a superior charge carrier mobility, high uniformity, and high reproducibility. A crystallization and growth mechanism of the bar-coated films and structure-charge-transport properties will be discussed.

UNDERSTANDING THE IMPACT OF BOTH THE ORGANIC SEMICONDUCTOR DESIGN AND PROCESSING CONDITIONS, ON BOTH MOLECULAR CONFORMATION AND THIN FILM MICROSTRUCTURE IS ESSENTIAL IN ACHIEVING THE REQUIRED OPTICAL AND ELECTRICAL PROPERTIES OF ORGANIC ELECTRONIC DEVICES. FOR EXAMPLE, THE CHARGE CARRIER MOBILITY IN AN ORGANIC FIELD EFFECT TRANSISTOR CAN BE SIGNIFICANTLY INCREASED THROUGH APPROPRIATE OPTIMIZATION OF THE SEMICONDUCTOR MOLECULAR CONFIGURATION AND SELF-ASSEMBLY. THESE ASPECTS WILL BE EXPLORED WITH AN INDACEO-NITRILEPHENOL AS A CASE STUDY. IT IS BELIEVED THAT CONFORMATIONAL DISORDER REDUCES CHARGE CARRIER MOBILITY IN ORGANIC ELECTRONIC DEVICES. UNDERSTANDING THE RELATIONSHIP BETWEEN THE MOLECULAR CONFIGURATION AND THE ELECTRICAL PROPERTIES IS CRUCIAL FOR THE DEVELOPMENT OF HIGH-MOBILITY ORGANIC ELECTRONIC DEVICES.
In order to solve these problems, we proposed the utilization of the liquid crystallinity in the soluble crystalline OTFT materials on the basis of our previous research for liquid crystals as a crystalline organic semiconductor [1]. Liquid crystalline materials exhibit crystal phase up to 100 °C, i.e., liquid crystal phase shows over 100 °C. We propose a new fabrication technique for uniform and molecularly flat polycrystalline thin films by utilizing liquid crystalline thin films as a precursor for polycrystalline thin films [2]. In order to improve the thermal durability of the films, we propose to utilize new liquid crystalline materials exhibiting highly ordered liquid crystal phases such as smectic E (SmE) phase, which gives high thermal stability in the thermal process thanks to solid-like nature of the highly ordered liquid crystals [3]. In this presentation, we will show the good processability, high thermal durability of the film up to 200 °C, and high mobility over 10 cm²/Vs in polycrystalline thin films of 2-phenyl-7-octyl-bezotheniobenzothiophene (Ph-BTBT-10) as representative liquid crystalline materials [4]. Ph-BTBT-10 has highly and low ordered smectic phases of SmE and SmA, respectively. The polycrystalline thin films of Ph-BTBT-10 fabricated by spin-coating at 110 °C for SmE phase were very uniform without any crystal flakes and cracks and the surface of polycrystalline thin films existed terrace structure with molecular step of ca. 3 nm that corresponds to a molecular length of Ph-BTBT-10. The polycrystalline thin film of thermal stability is much improved. The thin films unchanged after the thermal stress at 200 °C, thanks to the solid-like nature of SmE phase up to 210 °C. The FET devices after thermal stress at 200 °C, thanks to the solid-like nature of SmE phase were improved with the conductivities of up to 7.5 S/cm. These results show how effective the SmE phase is to improve thermal durability of OTFT in BTBT derivatives. Polycrystalline thin films of Ph-BTBT-10 show high mobility over 10 cm²/Vs after short thermal annealing at 120 °C at cryo phase. The polycrystalline thin films changed from monolayer to bilayer crystal structures after the thermal annealing and the utilization of bilayer crystal films via monolayer crystal films is good idea to realize for fabrication of uniform thin film by solution process and high mobility of bilayer crystal structure.

Device Performance of Polycrystalline Ph-BTBT-10 OFETs Solution-Processed Under a Low Voltage and Bias-Stress Conditions

[1] Ichi Hanna; Tokyo Institute of Technology, Yokohama, Japan.

2:30 PM EP01.02.03
Improved Molecular Order and Conductivity in Fulleren Derivatives by Tailoring the Side Chain

Jian Liu, Bas Zee, Jingjin Dong, Li Qiu, Giuseppe Portale, Jan C. Hummelen and Lambert Jan Anton Koster; University of Groningen, Groningen, Netherlands.

Organic semiconductors have attracted increasing attention as low-temperature thermoelectric materials, offering the possibility of fabricating low-cost, large-scale and mechanically flexible thermoelectric modules. The thermal conductivity of organic semiconductors is intrinsically low, leaving the power factor as the most important parameter for optimization. The widely used strategy to optimize power factor, molecular doping, enables an increase in electrical conductivity, but usually at the cost of reducing the Seebeck coefficient. Molecular ordering, which is typically low in a doped organic semiconductor, can improve the electrical conductivity and, hence, the power factor. However, there is no universal strategy to induce a disorder-to-order transition in a doped organic film.

In this contribution, we demonstrate that the molecular order of pristine and doped fulleren derivatives can be greatly improved by a suitable choice of the side chain. We use a fullerene derivative with two oligo ethylene glycol side chains, PTEG-2. Annealing induces a significant ordering in thin films of this material. After cooling back to the room temperature, the ordered form of PTEG-2 remains. GIWAXS data show that the molecular order is significantly enhanced after thermal annealing, leading to very promising results that may lead to the use of PTEG-2 as a new material for optoelectronic applications, with increasing resulting in conductivities of up to 7.5 S/cm. Additionally, this structural transition does not greatly influence the Seebeck coefficient, and leads to a power factor of up to 25 μWm⁻²K⁻². Finally, doped PTEG-2 films are very stable during annealing at 150 degree Celsius, which is of importance in thermoelectric applications. Our work introduces an effective strategy for improving molecular order and thus n-type organic thermoelectric performance.

2:45 PM EP01.02.04
Device Performance of Polycrystalline Ph-BTBT-10 OFETs Solution-Processed Under a Low Voltage and Bias-Stress Conditions

Masaumi Kunii, Hiroaki Ito and Jun-Ichi Hanna; Tokyo Institute of Technology, Yokohama, Japan.

Organic field effect transistors (OFETs) have attracted high attention in the past decades for its potential in industrial applications such as flexible displays, organic bio-medical sensors, and flexible radio frequency identification (RFID) tags. In fact, among various OFET materials so far proposed, some of which exhibited high OFET mobility over a few cm²/Vs. However, FET performance have hardly been investigated in detail where practical device performance are concerned such as OFET characteristics under low voltage driving and high bias-stress stability. In this study, we evaluated OFET performance fabricated with solution-processed polycrystalline thin films of liquid crystalline organic semiconductor of 2-phenyl-7-decyl-[1]benzothenio[3,2-b][1]benzotheniophene (Ph-BTBT-10) under the low voltage and high bias-stress conditions described above.

Ph-BTBT-10 OFETs (bottom-gate and bottom-contact FET with W/L of 350 μm/70μm) were fabricated with low-k polyamide/SiO₂ hybrid gate dielectric using highly ordered smectic E (SmE) liquid crystalline phase, which helps organic molecules form a well-aligned crystaline thin film during spin-coating process and gives it high thermal stability.
The transfer characteristics were measured at drain voltage ($V_D = -0.1$ V for linear regime and at $V_D = -2$ V for saturation regime) under ambient air at room temperature. Despite the polycrystalline nature of Ph-BTBT-10 and low-$\kappa$ gate dielectric, the solution-processed, bottom-gate, bottom-contact Ph-BTBT-10 OFET exhibits saturation mobility up to 4.9 cm$^2$/Vs with the subthreshold swing of 79 mV/decade, which is very close to the theoretical limit of 60 mV/decade at room temperature [1].

On the other hand, we evaluated OFET bias-stress stability that depends on gate voltages as a function of operation time up to 10$^3$ s. The negative gate bias-stress caused negative threshold voltage shift ($\Delta V_T$) for Ph-BTBT-10 FET in ambient air, but $\Delta V_T$ rapidly decreases as the gate bias decreases and approaches to near zero when the gate bias went down to 0V in amplitude. In contrast, positive gate bias-stress causes negligible $\Delta V_T$ even with a relatively high bias voltage [2]. All these results conclude that Ph-BTBT-10 FET has excellent FET performance at a low voltage operation as well as excellent bias-stress stability in ambient air in the range of low to moderate operating voltages.

References:

SESSION EP01.03: Transport I
Session Chairs: David Jones and Alberto Salleo
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 221 A

3:30 PM *EP01.03.01

Energetics and Transport in Ordered Mesophases of Organic Semiconductors—Implications for the Solar Cells Performance

Denis Andrienko$^{1,2}$, Max Planck Institute for Polymer Research, Mainz, Germany; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

We discuss the role of mesoscale order, electrostatic effects, defects, and roughness for charge splitting and detrapping at organic–organic interfaces. We show how inclusion of mesoscale order resolves the controversy between experimental and theoretical results for the energy-level profile and alignment in a variety of photovoltaic systems, with direct experimental validation [1,2]. We also show how one can predict open circuit voltages of planar heterojunction solar cells, in excellent agreement with experimental data, based only on crystal structures and interfacial orientation. We explain how long-range molecular order and interfacial mixing generate homogeneous electrostatic forces that can drive charge separation and prevent minority carrier trapping across a donor-acceptor interface [2]. Comparing several of small-molecule donor-fullerene combinations, we illustrate how tuning of molecular orientation and interfacial mixing leads to a trade-off between photovoltaic gap and charge-splitting and detrapping forces, with consequences for the design of efficient photovoltaic devices. By accounting for long-range mesoscale fields, we obtain the ionization energies in both crystalline [3] and mesoscopically amorphous systems with high accuracy [4,5,6,7].

References:

4:00 PM *EP01.03.02

Charge Transport in Diareno-Fused Antiaromatic Molecules

Andrew Zeidell$^1$, Laura Jennings$^2$, Coned K. Frederickson$^1$, Qianxiang Ai$^1$, Chad Risko$^2$, Michael M. Haley$^2$ and Oana Jurchescu$^1$; $^1$Department of Chemistry & Biochemistry and the Materials Science Center, University of Oregon, Eugene, Oregon, United States; $^2$Department of Chemistry, University of Kentucky, Lexington, Kentucky, United States; $^3$Max-Planck Institute for Polymer Research, Mainz, Germany; $^4$King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Charge transport in organic semiconductors is strongly related to the molecular structure and the solid-state packing within the crystal. Reducing molecule aromaticity, while preserving conjugation length, can be effective in enhancing carrier mobility. One example of such a system is the diareno-antiaromatic compounds. In this study, we synthesized a series of dinaphtho-fused x-indacenes and evaluated their electronic and electrical properties using a combined computational and experimental approach. Three different substitutions of the linear fused dinaphthindacene (DNI) backbone were investigated, namely (n-octylidiosopropylisilyl)ethyl nODIPS, (tris(isobutylisilyl)ethynyl)TIBS, and (tris(isopropylisilyl)ethynyl)TIPS. Computational studies find high effective masses in the nODIPS and TIBS derivatives, suggesting that the charge transport is not effective in these materials. On the contrary, the TIPS substituted molecule yielded low effective masses for both holes and electrons, indicating that charge carrier mobility can be high in this compound. To test the electrical properties of these semiconductors, thin films of each derivative were electrically characterized in a top-gate bottom contact field effect transistor architecture. Gold and silver, in combination with several chemical treatments, served as source and drain electrodes, while spin-coated Cytop fluoropolymer was the dielectric. To improve thin film morphology and crystallinity, a solvent vapor annealing post-processing step was employed. The TIPS and nODIPS derivatives did not yield working devices, in agreement with the theoretical predictions. In the TIPS-substituted DNI, we measured hole mobilities as high as 2.25 cm$^2$/Vs, in agreement with the low effective mass of 0.52 m, and over three times larger than the mobility measured in the linear isomer. We were not able to detect unipolar electron transport, in spite of the low electron effective mass of this compound (0.43 m), most likely because of inefficient injection from the high work function electrodes and trapping at the semiconductor/dielectric interface. Our results underline the importance of fine-tuning the molecular structure in order to obtain high mobility organic semiconductors.

4:15 PM EP01.03.03

Effect of Static Disorder Comparable to Dynamic Disorder on Charge Transport in Liquid Crystals

Akira Ohno, Jun-Ichi Hanna and Hiroaki Iino; Tokyo Institute of Technology, Yokohama, Japan.

During the past decade, many new candidates of organic semiconductors exhibiting not only performance (high mobility exceeding over 10 cm$^2$/Vs) but also stability (thermal stability or lifetime etc.) or processability (printable or low-cost process) have been fabricated and developed significantly in response to various demands of device performance. However, there is no general solution to satisfy both performance and structural stability. Our approach to using liquid crystallinity is one of the candidates for the general solution. Introducing partial disorder of liquid crystallinity for the device fabrication is to accept the fluidity of the material and to provide the large- and uniform- thin film without structural defects or grain boundaries, which extrinsically cause serious problems for charge transport. On the other hand these partial disorder and fluidity provide static disorder ubiquitously distributed. For example, the degree of freedom in alkyl chain or flip-flop motion of p-conjugated core, which are typical behavior of “high-ordered” liquid crystal. In our research, we focus on these static disorders which are inherent in liquid crystals. We discuss these static disorders using the theoretical estimation and the simulation compared with experimental results for phenyl naphthalene, biphenyl, the thiophene and BTBT derivatives exhibiting smectic E phase which is typical phase using for device process we are proposing. We found that these disorders are controlled by order parameters of liquid crystallinity because they are not extrinsic origin but intrinsic disorder caused by the degree of freedom originated by liquid crystallinity. These typical values of disorder (typically ~50meV in energetic disorder) in liquid crystal are small compared with those in amorphous (~100meV). However, they are not ignored and their activation energy is comparable with polaron binding energy. Thus their transport behavior is the superposition of small polaron and Gaussian disorder effects.
In introducing side chains into the phthalocyanine (Pc) molecule to induce liquid crystalline (LC) phases, there are two types of molecular structures, namely, a peripheral type and non-peripheral type. We have investigated the molecular packing and electronic transport characteristics of mesogenic Pc having alkyl side chains at non-peripheral sites, 1,4,8,11,15,18,22,25-octaalkylphthalocyanine (CnPc), and their families. These compounds exhibit very high long-range drift mobility up to 1.4 cm²/Vs evaluated by time of flight measurement and must be a candidate of organic semiconductor for printable electronics [1,2]. However, this fact is contrary to expectation. Namely, it can be easily predicted that the planarity of the Pc molecular plane might be reduced due to large steric hindrance between non-peripherally substituted chains and disordered molecular stacking undesirable for carrier transport is formed.

We have also demonstrated a high-efficient bulk-heterojunction (BJH) solar cell based on C6PcH and their family, which shows a high power conversion efficiency of 5.3% [3-5]. For the formation of the optimally phase-separated nano-structure for efficient carrier generation and transportation, the mesogenic properties should play an important role. Using self-organizing characteristics of LC phase, we can fabricate a large area monodomain thin film of CnPc for electronic devices. A well-aligned uniaxial single crystal growth in large area of printed thin film was obtained by means of conversion process from LC phase in a supercooled state to crystal phase. CnPc shows a crystal polymorphism and forms two different crystal structures (α-phase or β-phase) depending on the growth condition of the crystal. The high mobility of C6Pc reported so far is evaluated in the crystal structure of the β-phase. However, according to the theoretical prediction, higher mobility is expected in the α-phase [6]. We have demonstrated a large area single crystaline film of α-phase converted from spin-coated β-phase Pc film, which is based on the crystal polymorphism conversion triggered by the solvent vapor treatment [7,8].

Acknowledgment
This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (17K18882, 18H04514), and by Advanced Low Carbon Technology Research and Development Program from the Japan Science and Technology Agency (JST-ALCA).

References
Benzothiophen[3,2-b]-[1]benzothieno[3,2-b]thiophene (BTBT) derivatives are very promising candidates in the field of solution processable organic semiconductors. In this work the surface crystallization behaviour of Ph-BTBT-T-10 is investigated. Thin films starting from the monolayer regime up to thick films were prepared by spin coating and physical vapour deposition. The films were investigated in terms of crystalline properties and thin film morphology by X-ray diffraction, X-ray reflectivity and Grazing Incidence X-ray diffraction, atomic force microscopy and optical microscopy. It is shown that by spin coating at low concentrations of 0.3 g/l an incomplete monolayer of standing molecules with the aromatic core pointing towards the substrate is formed. At higher concentrations between 0.5 g/l and 3 g/l strong island growth starts which leads to the formation of macroscopic islands with dendritic monolayers in-between them. Physical vapour deposition demonstrates a more homogenous distribution of the material forming terraces of multiple molecules. In thin films whether in solution (5 g/l) or PVD (300 Å) crystalline structures are observed in XRD. As well as the known bulk phase with a head to head arrangement of two molecules in an orthorhombic unit cell possessing a herringbone structure, also other polymorphic phases are present.

Recent advances in organic solar cell ingredients and processing have enabled fabrication of single devices with power conversion efficiencies in excess of 15%. However, such high efficiencies are not realized in commercial products because of the difficulty scaling up robust self-assembly of the active layer components. For mass-produced devices to be commercially viable, the factors governing self-assembly of structure, and how that structure determines charge transport must be understood. Investigating these factors is challenging due to the multiplex combinations of chemistries and processing protocols that are feasible. However, searching these combinations can be accelerated through the use of computational tools such as molecular dynamics and kinetic Monte Carlo. In this work, we develop an united-atom model for the benchmark donor polymer poly-(3-hexylthiophene), resulting in the most experimentally accurate structures to date. We then predict the self-assembly and charge transport under hundreds of processing variable combinations. We find that ordered structures obtained using good solvents allow for the highest charge transport rates. Furthermore, we find that polymer ‘tie-chains’, which span between crystallites, are critical in preventing charges from becoming trapped within local structural features. We discuss modeling successes with more complex molecules and demonstrate promise for these tools in developing design rules for mass producing organic solar cells.

High-Performance Ternary Organic Solar Cell Enabled by a Thick Active Layer Containing a Liquid Crystalline Small Molecule Donor Fei Huang; South China Univ of Technology, Guangzhou, China.

Recent advances in organic solar cell ingredients and processing have enabled fabrication of single devices with power conversion efficiencies in excess of 15%. However, such high efficiencies are not realized in commercial products because of the difficulty scaling up robust self-assembly of the active layer components. For mass-produced devices to be commercially viable, the factors governing self-assembly of structure, and how that structure determines charge transport must be understood. Investigating these factors is challenging due to the multiplex combinations of chemistries and processing protocols that are feasible. However, searching these combinations can be accelerated through the use of computational tools such as molecular dynamics and kinetic Monte Carlo. In this work, we develop an united-atom model for the benchmark donor polymer poly-(3-hexylthiophene), resulting in the most experimentally accurate structures to date. We then predict the self-assembly and charge transport under hundreds of processing variable combinations. We find that ordered structures obtained using good solvents allow for the highest charge transport rates. Furthermore, we find that polymer ‘tie-chains’, which span between crystallites, are critical in preventing charges from becoming trapped within local structural features. We discuss modeling successes with more complex molecules and demonstrate promise for these tools in developing design rules for mass producing organic solar cells.

Inverted thermal activation of charge mobility in polymer field effect transistors (FETs) has been recently observed in a few cases for holes and in a single case only for electrons. Such exciting observations lead us to foresee a future of polymer FETs beyond hopping transport limitations. Yet, there is a clear lack of understanding of the fundamental reasons leading to such transport regime and, as a consequence, of synthetic and processing guidelines. Here we make use of uniaxial molecular alignment and specific thermal treatments within the melting endotherm of a diketopyrrolopyrrole-tetrafluorobenzene-based electron transporting copolymer films to induce a favorable microstructure for electron transport. Thanks to such strategy we can achieve a single-crystal like, voltage independent mobility, with vanishing activation energy close to room temperature. We make use of extensive microstructural, electrical, electro-optical and theoretical investigations to rationalize the transition from a hopping to a band-like transport regime, and link it to the microstructure. Thermal barriers present in the disordered phase can be effectively suppressed in the direction of molecular alignment by a more efficient interconnection of the ordered phase following the increased crystals extension occurring during the thermal process.

SESSION EP01.06: Transport II
Session Chairs: Jun-Ichi Hanna and Elizabeth von Hauff
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 221 A

1:30 PM *EP01.06.01
Polaron Delocalization and Mesoscale Effects in Charge Transport in Semicrystalline Conjugated Polymers Alberto Salleso; Stanford University, Stanford, California, United States.

Typically semicrystalline conjugated polymers exhibit much higher mobility than their amorphous counterpart. The archetypical example is regio-random P3HT, with mobilities on the order of 10−6 cm2/V.s as compared to regio-regular P3HT with mobilities on the order of 0.1 cm2/V.s. The oft-cited reason for these differences is the fact that in polymer crystallites charges delocalize and take a partial 2D character, enabling higher mobility. The amount of delocalization and how it depends on structure and processing is however difficult to measure. We will show that charge modulation spectroscopy in the IR with model materials allows to determine the delocalization of the polaron in P3HT when aided by theory. In order to extract systematic trends we will use 100% regio-regular P3HT of well-defined molecular weights (PDF−1.1). These model materials allow to clearly discern different limiting factors in charge transport and how they depend on molecular weight. On one hand, short polymer segments crystallize well but have torsional disorder, which localizes the charges in 1D. As the molecular weight increases, backbone torsion decreases and charges delocalize in 2D. Eventually delocalization saturates and mobility increases are attributed to connectivity between crystallites. We extend this framework beyond model materials and study charge delocalization in high-performance donor-acceptor polymers and aligned polymers for stretchable electronics. In aligned films we are able to directly measure delocalization along the backbone and across molecules.

2:00 PM *EP01.06.02
Nematic Interactions, Ordering and Effects on Charge Mobility in Semiconducting Copolymers Scott T. Milner; The Pennsylvania State University, State College, Pennsylvania, United States.

Organic semiconducting polymers are typically rather stiff compared to traditional polymers, because the monomers are aromatic rings, and the deflection angle between successive rings is small. This leads to the possibility of significant nematic interactions between chains in an isotropic melt just from steric considerations. Working against this tendency are the solubilizing sidechains, which dilute the stiff backbones with flexible “grease”. In recent work, we have used atomistic simulations to predict the nematic coupling constant alpha for semiconducting polymers such as P3HT, and predicted the isotropic-nematic (IN) transition temperature. Our method does not rely on observing the nematic ordering transition with its attendant slow kinetics, but instead infers alpha from its amplifying effect on the elongation of chains in an isotropic melt in response to an applied
external tension. Even when alpha is not large enough to result in a stable nematic phase, nematic interactions can amplify the aligning effect of an impenetrable surface, at which semiflexible chains tend to lie parallel. We have investigated this effect with coarse-grained MD simulations of melts near a wall, in which we observe how far nematic order extends from the wall into the bulk, as a function of chain stiffness. These results compare well to our predictions from self-consistent field calculations adapted to semiflexible chains. We have exploited this surface alignment effect to locate the IN transition, by observing how surface alignment propagates into a slab of polymer chains confined between walls, as the chain stiffness increases. Below the IN transition, surface-induced alignment grows into the bulk with a velocity proportional to the undercooling. By observing how the front propagates as we cool (or increase chain stiffness), we can accurately locate the transition.

Nematic order is important in semiflexible polymers because electronic transport in semiflexible polymers is inherently anisotropic. Conformers move readily along straight chains, which can hop with relative ease between parallel chains in a crystal, and hop only with difficulty between obliquely oriented chains in an isotropic melt. Crystallization from a nematic phase may give better-organized crystalline domains with fewer amorphous regions, and may induce chain alignment even in the amorphous regions. In a separate thrust of our research, we have developed coarse-grained electronic models capable of describing carrier states and motion in crystalline and amorphous semiflexible polymers such as P3HT. Our approach uses tight-binding models, in which each ring moiety is a site, with hopping between adjacent sites. Parameters are tuned to agreement with state-of-the-art DFT calculations for small systems in well-defined geometries. Hopping matrix elements along chains are large for trans dihedrals, but fall off and vanish as dihedrals rotate to 90 degrees, breaking conjugation. Conformers in P3HT form polars, in which the surrounding material reorganizes (“polarizes”) in response to the presence of the charge. The polaron size is set by a competition between electronic kinetic energy (which seeks to delocalize the charge) and the reorganization energy (which stabilizes a localized charge more effectively). The most important contribution to reorganization energy in these materials is dielectric polarization of nearby material, leading to polarons a few rings long. These polarons can move between chains a crystal, by hops described by Marcus theory. In the hopping barrier state, the polaron is midway between two degenerate locations, in a symmetric superposition of states. We use our tight-binding model to compute barriers for hopping between chains, in a crystal and an amorphous melt. The melt barrier is larger, because obligiously oriented chains do not share very effectively the same polarization field, which increases the reorganization energy.

3:00 PM SESSION: EP01.07: Material Design and Fabrication III

3:30 PM *EP01.07.01 Electronic Functions in Liquid-Crystalline Nanostructures with High Polarization Masahiro Funahashi1,2; 1Department of Advanced Materials Science, Kagawa University, Takamatsu, Japan; 2Health Research Institute, National Institute of Advanced Industrial Science and Technology, Takamatsu, Japan.

Nanosegregated \( \pi \)-conjugated liquid crystals can be multi-functional soft materials in which an electronic function couples with optic, ionic, ferroelectric, and electrochemical activities. In this study, we demonstrate the coupling of electronic function with ionic transport and ferroelectricity in the columnar and chiral smectic C\(^\ast\) (SmC\(^\ast\)) phases, respectively. Strong electric field based on the polarization of electrolytes and spontaneous polarization of ferroelectrics can produce various electronic functions.

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Quantitative Analysis of the Density of Trap States in Organic Semiconductors by Current-Voltage Measurements on Low-Voltage Thin-Film Transistors

Michael Geiger1, Lukas Schwarz2, Ute Zichesichang2, Dirk Manske1, Jens Pflaum1, Jürgen Weis2, Hagen Klauck2 and Thomas Weitz2,3,4

1Max Planck Institute for Solid State Research, Stuttgart, Germany; 2Faculty of Physics, Ludwig-Maximilians-Universität München, München, Germany; 3Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, München, Germany; 4Nanosystems Initiative Munich (NIM) and Center for NanoScience (CeNS), Ludwig-Maximilians-Universität München, München, Germany.

The electrical characteristics of thin-film transistors (TFTs) based on disordered semiconductors, such as hydrogenated amorphous silicon, metal oxides and conjugated organic semiconductors, are greatly influenced by the density and energetic distribution of localized electronic states in the energy gap of the semiconductor arising from chemical or structural defects. In the 1980s, Grünewald et al. developed a method to convert a measured transfer curve of a field-effect transistor to the underlying density-of-trap-states (trap DOS) function [1]. Solvent vapor annealing [2] involving swelling and recrystallization of as-cast films allows to control nucleation densities and to grow sphere-like superstructures. Interestingly, the sphere-like superstructures result from radial growth of fibers with the fiber growth direction being the polymer chain direction. Simple blade coating from concentrated solutions even yields square centimeter large oriented films – again made of fibers - with dichroic ratios of 18 and charge transport anisotropies up to 14. Nucleation and growth mechanisms can be understood in terms of a reorientation of pre-formed aggregates in solution, suggesting nematic-like preorientations. These findings show completely different growth behavior than previously developed for the well-studied p-type polymer poly(3-hexylthiophene) [3].

The influence of regioregularity on aggregation behavior [4] and on chemical and electrochemical doping performance will be also discussed during the presentation [5].

Grazing incidence X-ray diffraction (GIXD) is an experimental method frequently applied to characterize a wide variety of thin films and surfaces. Depending on the texture of the surface's crystallites, special care is required during the experimental measurements and successive data evaluation. For example, samples with large individual crystallites on a surface resulting in poor statistics or epitaxially grown samples with defined in-plane alignment of the crystallites require both a full sample rotation around the surface normal during data collection. This is necessary to obtain all information for phase, texture and epitaxy analysis. Moreover, this experimental approach opens new possibilities for advanced characterisation methods which in simple static experiments are inaccessible, e.g. the determination of the in-plane mosaicity. GIDVis is a software package developed in MATLAB for visualization and analysis of GIXD data in general but mostly used for thin films. It is specialized on data obtained during a sample rotation around the surface normal, i.e. a rotating GIXD experiment. Due to the geometrical independent character of the underlying algorithms implemented, most features can be used independently from the input data type. GIDVis allows the user to perform detector calibration, data stitching, intensity corrections, standard data evaluation (e.g. cuts and integrations along specific reciprocal space directions), crystal phase analysis, etc. Further, these features are not limited to a single experimental setup, data from mostly all diffraction setups can be processed. To fully take advantage of the measured data in the case of sample rotation, pole figures can be calculated from the experimental data for any q value covered. As an example, GIDVis is used here to investigate the epitaxial alignment of pentacenequinone (P2O) crystallites on a Au(111) surface, illustrating the importance of the sample rotation. GIDVis is available online free of charge (http://www.if.tugraz.at/am/GIDVis/).

Remote-Controllable Actuating and Rewritable Films Fabricated by Self-Assembled Hierarchical Superstructure Kwang-Un Jeong, Dayoung Jung, Hyeeyoon Ko and Minwoo Rim; Chonbuk National University, Jeonju, Korea (the Republic of).

Benzene-1,3,5-Tricarboxamide Macrogelator Kwang-Un Jeong, Seungchul Yang, Geukcheon Bang; Dayoung Jung, Hyeeyoon Ko and Minwoo Rim; Chonbuk National University, Jeonju, Korea (the Republic of).

Remote-Controllable Electro-Optical Device—Liquid Crystal Physical Gel Fabricated from Benzene-1,3,5-Tricarboxamide Macrogelator Kwang-Un Jeong, Seungchul Yang, Geukcheon Bang; Dayoung Jung, Hyeeyoon Ko and Minwoo Rim; Chonbuk National University, Jeonju, Korea (the Republic of).

Dual-Responsive Electro-Optical Device—Liquid Crystal Physical Gel Fabricated from Benzene-1,3,5-Tricarboxamide Macrogelator Kwang-Un Jeong, Seungchul Yang, Geukcheon Bang; Dayoung Jung, Hyeeyoon Ko and Minwoo Rim; Chonbuk National University, Jeonju, Korea (the Republic of).

The Software GIDVis and Its Application to the Evaluation of Rotating Grazing Incidence X-Ray Diffraction Experiments Benedikt Schröde1, Stefan Pachmajer1, Michael Doehl, Christian Röthel, Jari Dornke, Roland Resel and Oliver Werzer2; 1Institute of Solid State Physics, Graz University of Technology, Graz, Austria; 2Institute of Pharmaceutical Sciences, Department of Pharmaceutical Technology, University Graz, Graz, Austria; 3Institute of Solid State Physics, Friedrich Schiller University Jena, Jena, Germany.

Flexible TFP showed excellent mechanical and chemical stability. Patterned and flexible TFP can drive the flexible devices market to a new level. This work was supported by BK21 Plus program, the BRL 2015042417, Mid-Career Researcher Program (2016R1A2B2010141).

To develop an advanced thermal interface material (TIM) which can effectively dissipate the problematic heat in the electronic devices, rod-shaped reactive mesogen (RM) was newly synthesized as a building block for the thermally conductive liquid crystal (LC) films. Based on the combined techniques of spectroscopy, scattering and thermal analyses, it was verified that the synthesized RM formed a smectic A (SmA) mesophase between crystalline and isotropic (I) phases. The thermal conducting LC films were fabricated by the photopolymerization of RM in both LC and isotropic phases. Regardless of the molecular packing structures, the thermal conducting LC films exhibited outstanding heat transfer properties over 1 W/mK that surpass the conventional polymeric materials. In addition, the heat conducting performance of LC film can be amplified in a certain direction by the uniaxial orientation of LC molecules in the network. The uniaxially oriented LC film exhibited significant heat guiding performance as TIM than that of conventional organic materials. The highly thermal conducting LC films can be used as an advanced thermal managing material for electronic devices. This work was supported by BK21 Plus program, the BRL 2015042417, Mid-Career Researcher Program (2016R1A2B2010141).

PDI-RM TFP exhibited the property of E-type polarizer with a polarizability of 99.81% at 491 nm (λmax). In addition, the patterned TFP showed excellent mechanical and chemical stability. Patterned and flexible TFP can drive the flexible devices market to a new level. This work was supported by BK21 Plus program, the BRL 2015042417, Mid-Career Researcher Program (2016R1A2B2010141).
Organic electronics offer the premise of low-cost, versatile electronic devices with alternative mechanical, optoelectronic, and chemical properties not afforded by inorganic semiconductors. One of the major limitations continues to be lower conductivity associated with their highly disordered systems. The predominant approach is to use chemical additives (i.e. dopants) that undergo charge transfer with the matrix organic semiconductor to increase carrier concentration and conductivity. Yet, broad application of doping has been limited as precise control has remained elusive, due to partial electron transfer events and/or phase segregation of dopant. Alternatively, electrochemical doping precisely varies conductive polymer properties with only an applied voltage on a thin film in an electrolyte. This allows for direct monitoring of the conductivity and holes/molecules in situ to evaluate critical structure-property relationships. As a proof of concept, and comparison to known chemical doping strategies, the model system poly(3-hexylthiophene) (P3HT) was held at different doping (oxidizing) potentials and subsequent doping effects were characterized using a combination of electrochemical and spectroscopic methods.

Conductivity was demonstrated to vary by ~10^3 from 2x10^4 S/cm for the undoped film exposed to electrolyte to 0.35 S/cm for the highly doped film in solution, with solid state conductivity being retained at 0.24 S/cm. UV-vis absorbance data confirms the presence of both polaronic and bipolaronic levels in the solution doping, although the bipolaronic species are not retained in the solid state. Complementary grazing incidence wide angle x-ray scattering (GIWAXS) demonstrates a voltage-dependent swelling of the film with increasing oxidation potential in the alkyl stacking direction, demonstrating preferential ion uptake while retaining the desired π-π stacking necessary for high electronic transport. These results demonstrate a promising alternative path to increasing conductivity of organic semiconductor films and could eliminate the synthetic bottleneck associated with designing dopants for individual semiconductor systems.

EP01.08.09
Reversible Doping in Organic Electronics—A Strategy to Finely Tune Electrical Conductivity

Jonathan Harriss, Bharati Neelamraju and Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Optical and Structural Anisotropy in Pentacene Thin Films Revealed by pMAIRS

Nobutaka Shiyo, Takafuli Shimosa and Takeshi Hasegawa; Institute for Chemical Research, Kyoto University, Uji, Japan.

Pentacene is one of the most basic materials in organic thin-film transistors. The compound is known to form a polycrystalline thin film, in which the molecular long axis is oriented perpendicular to the substrate surface, i.e., end-on orientation. The face-on oriented thin film, on the other hand, where the molecular plane is parallel to the substrate, has never been found on an inert substrate represented by SiO2. As a result, the face-on orientation has long been believed to be generated only on specific substrates such as a metal single crystal.

A low-temperature (LT) deposition technique is suitable for obtaining the metastable face-on crystalline film on an inert substrate. In a low temperature region (<223 K) of the substrate, however, pentacene molecules have long been believed to take a randomly oriented amorphous structure.

In the present study, the LT film of pentacene is re-investigated by using p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) together with two-dimensional grazing incidence X-ray diffraction (2D-GIXD). The combination of the cutting-edge techniques readily reveals that the face-on phase is definitely realized as the dominant component. In short, the present study shows that the conventional schematic of the “amorphous” structure should be revised.

EP01.08.10
Controlling Solution Assembly Behaviors of P3HT-b-P2VP Block Copolymers via Tuning Regioregularity

Younseok Kim1, Hyoeng J. Kim2, Jin-Seong Kim2, Hongseok Yun1, Hyoemyung Park1, Junghun Han1 and Bumjoon J. Kim3; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2University of Massachusetts Amherst, Amherst, Massachusetts, United States.

In selective solvents, poly(3-hexylthiophene) (P3HT)-based block copolymers (BCPs) assemble into crystallized nanowire (NW) structures due to the strong crystalline interactions of the rigid P3HT block. Herein, we report the effect of the crystalline interactions of the P3HT block on the self-assembled structure of the P3HT-based BCPs in solvent by modulating the regioregularities (RRs) of P3HT. We synthesized a series of P3HT-block-poly(2-vinylpyridine) (P3HT-b-P2VP) copolymers that had the same molecular weights but various RRs, ranging from 55 to 95%, and we investigate their behavior in a binary solvent mixture. We observed a remarkable transition from the well-defined 1D NW structure to micelle structures (i.e., spherical micelles) depending on RR. The well-defined NW structures were produced from the P3HT-b-P2VP copolymers with high RR, i.e., 95%. For the RR of 55% in the BCPs, crystallization of the P3HT moiety was suppressed so that only micelle structures were formed. Remarkably, between RR values of 75% and 65% in the BCPs, we observed 1D nanostructures, which are considered to be intermediate morphologies between NWs and micelles. Even though they had distinctive characteristics, such as larger widths and heights, less crystalline properties, and different positions of the P2VP chains than conventional NWs, they still possessed partial crystallinity, which was different from the amorphous assemblies of RR of 55% BCPs. Therefore, we demonstrated the substantial relationships between the solution assembly behaviors and the crystalline interactions of conjugated semicrystalline–coil BCPs, which can be used as important guidelines for designing versatile BCP nanostructures.

EP01.08.12
Discrete Monolayers of a Benzothieno-benzthiophene Derivative at Silicon Oxide Surfaces—Structures Formed by Liquid Crystalline States

Michael Dohr1, Oliver Werzer2, Quan Shen3, Christian Teichert4, Yves Geerts5, Michele Sferrazza6 and Roland Resel1; 1Graz University of Technology, Graz, Austria; 2Institute of Pharmaceutical Sciences, Graz University, Graz, Austria; 3Institut für Physik, Montanuniversität Leoben, Leoben, Austria; 4Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium.

During the last years the molecule diocetyl-benzothienobenzothiophene (C8-BTBT-C8) has attracted large attention, since thin film transistors based on this organic semiconductor show outstanding device performance. The high quality of the C8-BTBT-C8 films may be one of the key features for the successful application. The presence of a liquid crystalline smectic state at elevated temperatures together with a highly defined crystalline state at room temperature allows special film preparation methods of high structural perfection. Thin films of C8-BTBT-C8 in the monolayer (thin films) and in the multilayer regime (thick films) are prepared by spin coating, a method far from thermodynamic equilibrium. Heat treatment of the films results in strong islanding (for thick films). The structure of the organic films is investigated by temperature-dependent in-situ methods using atomic force microscopy, x-ray reflectivity, and grazing incidence x-ray diffraction [1]. Already at temperatures few degrees below the phase transition from the crystalline state to the smectic A state (T = 381.5 K), the formation of a single monolayer is observed. The molecular rearrangement takes 30 minutes until the monolayer formation is completed. In case of thick films an increase of the temperature in defined steps induces discrete monolayer formation as bi-layer, triple-layer, etc. Up to 5-layer structures are observed. The reversibility of the discrete layer formation reveals that thermodynamic equilibrium states are observed. Non-equilibrium structures can be stabilised by rapid cooling from the respective temperature [2]. Explanation of these observations are given in terms of the classical film formation models using surface energy of the used silicon oxide surface and the variation of the surface energies / surface tension of the molecule C8-BTBT-C8.


EP01.08.13
Optical and Structural Anisotropy in Pentacene Thin Films Revealed by pMAIRS

Nobutaka Shiyo, Takafuli Shimosa and Takeshi Hasegawa; Institute for Chemical Research, Kyoto University, Uji, Japan.

In short, the present study shows that the conventional schematic of the “amorphous” structure should be revised.
The crystal structures of Ph-BTBT-10 thin films were analyzed by thermal in situ 2D-GIXD at different substrate temperatures. The Ph-BTBT-10 films at RT and 60 °C showed a similar series of peaks assignable to a monolayer structure with a d-spacing of 27 Å. When the substrate temperature was increased to 120 °C, the diffraction peaks clearly changed, which suggests a transformation from a monolayer structure (d = 27 Å) into a bilayer structure with a d-spacing of 54 Å. Since the phase transition temperature to SmE (SmE) mesophase is 144 °C, a series of peaks assignable to SmE were observed when heated to 180 °C. In addition, a mixed layer of monolayer and bilayer structures appeared when the Ph-BTBT-10 thin film was rapidly cooled from 180 °C to RT. This result indicates that the cooling speed might be a significant factor in forming a well-uniformed crystalline thin film structure. Based on these results, Ph-BTBT-10 can be handled through vacuum deposition method, and the phase transition from the monolayer to the bilayer structure can occur in the same way which occurs for solution processed Ph-BTBT-10 thin films. Finally, we demonstrated top-ranked FET performances through vacuum deposition process. This presentation will also include fabrication and evaluation of Ph-BTBT-10-based device via dip-coating method.

1) H. Ino, T. Usui, J. Hanna, Nat. Commun. 2015, 6, 6828.

EP01.08.15 Understanding Molecular Aggregation of Emissive Guests in Organic Light-Emitting Diodes with Atom Probe Tomography Matthew Jaskot1, Andrew P. Proudnian2, Galen B. Vincent2 and Jeramy D. Zimmerman2; Materials Science, Colorado School of Mines, Golden, Colorado, United States; 2Physics, Colorado School of Mines, Golden, Colorado, United States.

In an organic light-emitting diode (OLED) device, the spatial distribution of dopant molecules in the emissive layer host-guest blend impacts key performance characteristics. Specifically, aggregation of dopant molecules is expected to exacerbate exciton annihilation processes associated with efficiency roll-off and device degradation. We have developed atom probe tomography (APT) techniques that allow us to create a chemically sensitive three-dimensional reconstruction of molecular positions (i.e. nanometer-scale spatial resolution with sub-Dalton mass discrimination). APT allows us to study dopant aggregation in OLED emissive layers based on a blend of multiple molecular constituents. We have used spatial statistics analysis of APT data to show that Ir(ppy)3 aggregates in a number of commonly used hosts; here, we investigate the effects of aggregation in an mCBP:Ir(ppy)3 emissive layer blend. By controlling substrate temperature during deposition, we show that we can control the spatial distribution of the dopant in the film. Hole mobility increases over two orders of magnitude in this system as substrate temperature increases from -50°C to 50°C (mCBP Tg = 97°C), which is consistent with the Gaussian Disorder Model and the assumption that holes are transported on the Ir(ppy)3: Highest Occupied Molecular Orbital (HOMO). We also show that the device triplet-triplet annihilation (TTA) rate increases with substrate temperature, as expected with stronger guest aggregation. Understanding how guest aggregation affects exciton dynamics and annihilation in an OLED emissive layer is an important step in maximizing device efficiencies and reducing the effects of long-term degradation.

EP01.08.16 Molecular Scale Patterning of Photonic Structures via Conformational Control Alice Smith1 and Donal D. Bradley1,2, 1Department of Physics, University of Oxford, Oxford, United Kingdom; 2Department of Engineering Science, University of Oxford, Oxford, United Kingdom.

Patterning structures at the scale of the wavelength of light is central to photonic device fabrication. Whilst standard patterning techniques such as e-beam lithography can be used to pattern the structure of any materials, orientation, configuration and conformation can also be used to control the optical properties of molecular materials. An example of conformation control is formation of the β-phase in the organic semiconductor poly(9,9-dioctylfluorene) (PFO), in which polymer chain segments adopt a rigid, planar structure when subjected to particular solvent interactions. The photophysics of this phase has been studied in great detail, with particular focus on the presence of a new long wavelength absorption peak, which results in a significant change in refractive index within the optical gap (10.9% at 450nm). The index change offers potential for photonic element fabrication, in a fashion that mimics dielectric metamaterial structuring on a molecular length scale. Spatial patterning of the structure defines the photonic elements, with millimeter scale patterning shown in 2009, followed by micron scale in 2012, and nanoscale in 2015. We now report a further study on the use of Dip Pen Nanolithography (DPN) - an AFM derived single step writing process - as a technique to pattern nanoscale structures and discuss their suitability for photonic device applications.

EP01.08.18 Phase Diagrams of poly(3-hexylthiophene):N,N’-alkyl Substituted Naphthalene Diimides Blends Dorota Chleboz1,2, Markus Mezger2, Gunnar Glaser2, Waldemar Goldmann1, Krzysztof Janus1, Kinga Danielowicz1 and Adam Kiersnowski1,3; 1Wrocław University of Science and Technology, Wrocław, Poland; 2Max Planck Institute for Polymer Research, Mainz, Germany; 3Leibniz Institute for Polymer Research, Dresden, Germany.

Fabrication of electronic devices based on organic semiconductors at the fundamental level can be considered a problem of engineering of polycrystalline materials. Tuning the charge transport properties in such materials requires controlling of size, perfection, distribution, and orientation of crystalline domains in the semiconducting films1. Those parameters can be controlled through film formation and post-processing conditions, such as thermal annealing. While the casting parameters (solvent, temperature etc.) exert an influence on the primary crystallization and formation of polycrystalline system, the annealing induces the further growth of crystalline domains, increases perfection of crystal packing but may also trigger phase transitions of the ordered phases crystallized from the solution. Insufficient insight into the processes occurring upon the annealing may lead to erroneous conclusions related to properties - especially when samples reveal a complex phase behavior like the one observed in the case of aromatic, conjugated molecules or polymers. These materials may show multiple packings in crystalline phases as well as multiple thermally-induced transitions between crystalline and liquid crystalline phases before reaching the isotropic state1. Different packing of molecules and hence different geometrical overlap of aromatic moieties may aﬀect charge transport properties. Thus in our research we concentrated on relationships between packing of molecules in the ordered domains and electronic properties of materials.

The study was focused on the blends of poly(3-hexylthiophene) (P3HT) with butyl- or hexyl- or octyl-substituted naphthalene diimides (NDI). In our experimental approach we have applied differential scanning calorimetry (DSC) to determine phase transition points and X-ray diffraction (XRD) to gain insights into the structure of molecular assemblies in the system. These studies were supplemented with images from scanning electron microscopy (SEM) providing information about the morphology of the blends. In order to correlate the structure and morphology with charge transport properties, the blends were tested in organic field effect transistors (OFETs). Results of our experiments indicated that packing of molecules in crystalline phases and mesophases as well as phase transition temperatures were related to molecular architecture of NDI and compositions of the blends. XRD and DSC data were used to determine phase diagrams for the blends of P3HT with NDI. It was found that decreasing content of NDI in the blends caused a notable decrease of the isotropization temperature of the NDI component. The melting point of P3HT also significantly drops as its content in the blend decreases. The profile of the isotropization points of the P3HT:NDI blends plotted as a function of composition revealed a clear minimum resembling the eutectic point. In some of the blends, we observed additional transitions that may suggest formation of new crystalline phases occurring neither in pure P3HT nor pure NDI. The studies of the blends by means of scanning electron microscopy indicated that composition of polycrystalline layers also exerted an influence on the crystalline morphology. The studies electronic properties in the model field-effect transistors (OFETs) revealed that the blends with the uniform, fine-grained polycrystalline morphologies enable balanced ambipolar charge carrier transport. This, once again, indicates that the fine tuning of the blends composition is crucial for engineering of organic electronic devices.

References

The work was supported by National Science Centre, Poland through the grant DEC-2016/22/E/ST5/00472

SESSION EP01.09: Material Design and Fabrication IV
Session Chairs: Enrique Gomez and Elizabeth von Hauff
Solution-Processed Photovoltaics—Opportunities Provided By Use of Material Science Tools

Natalie Stimpeling; Georgia Institute of Technology, Atlanta, Georgia, United States.

In the past decade, significant progress has been made in the fabrication of organic photovoltaic devices (OPVs), predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. Real understanding of what structural and electronic features determine, for instance, the short-circuit current (Jsc), open-circuit voltage ( Voc) and fill factor are still lacking; and the role of charge transfer states and which charge transfer states are critical for efficient charge generation are still debated. Here we attempt to obtain further insight of relevant structure/processing/performance interrelations using classical polymer processing “tools.” We present a survey on the principles of structure development of this material family and how it can be manipulated, with focus on how to control the morphology and important interfaces (molecular and between different phase regions). Goal is to tailor and tune the final “ morphology” towards establishing correlations with relevant device characteristics. Examples are given based on polymer:fullerene solar cells as well as solution-processed perovskite structures.

11:00 AM -EP01.09.02

Nanostructured Liquid-Crystalline Assemblies for Ion and Electron Transport

Takash Kato; Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo, Japan.

Nanostructured liquid-crystalline (LC) assemblies forming columnar, smectic, and bicontinuous cubic phases can provide 1D, 2D, and 3D nano-channels capable of transport of ion and electron [1,2]. We have developed these nanostructured functional soft materials. Potential applications of these materials as electrolytes electrochemical devices, luminescence materials, and semiconductors have been shown. Here we report design, self-assembled structures, and functions of nanostructured LC materials exhibiting ion and electron transport properties. Nanostructured ionic liquid crystals bearing imidazolium and ammonium moieties and liquid crystals complexed with ionic species exhibit 1D, 2D, and 3D ion transport properties. They can be used for electrolytes for lithium ion batteries [3-4] and photovoltaics [5]. They also show stimuli responsive properties such as conductivity switching [6] and photo-control of ion transport directions [7]. Electron transport LC materials have also been developed [8,9]. Supramolecular hydrogen-bonded electron transport materials exhibit ion recognition properties [9].

References:

11:30 AM EP01.09.03

Molecular Packing Dependent Photophysics and (Opto)electronic Properties of Functionalized Anthradithiophene Single Crystals

Jonathan Van Scheneck1, Gregory Giesbers1, Keshab Paudel1, John Anthony2 and Oksana Ostrovskov3; 1Oregon State University, Corvallis, Oregon, United States; 2Chemistry, University of Kentucky, Lexington, Kentucky, United States.

Organic semiconductors have attracted attention due to their relative ease of fabrication, cost economy, and uniquely tunable optical and electronic properties via functionalization of the molecules. These properties in the solid state are determined both by the molecular structure and molecular packing, and thus it is important to understand the contribution of each factor to the resulting performance of the material, although separating these contributions remains challenging. Towards resolving the challenge, we present a systematic study of the optical and optoelectronic properties of single crystals of fluorinated anthradithiophene (ADT) functionalized with various side groups R (diF R-ADT) that control the molecular packing.

The optical properties of isolated diF R-ADT molecules are dominated by those of the backbone of the molecule, irrespective of the side groups R. In the solid state, however, only extract the second moment of the transition dipole moment with respect to the film surface, leaving several possible configurations of the investigated molecule within a three dimensional space.

In the past decade, significant progress has been made in the fabrication of organic photovoltaic devices (OPVs), predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. Real understanding of what structural and electronic features determine, for instance, the short-circuit current (Jsc), open-circuit voltage (Voc) and fill factor are still lacking; and the role of charge transfer states and which charge transfer states are critical for efficient charge generation are still debated. Here we attempt to obtain further insight of relevant structure/processing/performance interrelations using classical polymer processing “tools.” We present a survey on the principles of structure development of this material family and how it can be manipulated, with focus on how to control the phase morphology and important interfaces (molecular and between different phase regions). Goal is to tailor and tune the final “ morphology” towards establishing correlations with relevant device characteristics. Examples are given based on polymer:fullerene solar cells as well as solution-processed perovskite structures.

Unraveling the orientation of emissive dye molecules within organic light-emitting diodes (OLEDs) is of crucial importance to achieve high performing devices. Within the last years vast progress has been made in understanding and predicting the preferential alignment of organic dye molecules using both experimental and computational methods. The most common technique to determine the orientation of the emissive species within a thin film is angular dependent photoluminescence spectroscopy. However this method can only extract the second moment of the transition dipole moment distribution with respect to the film surface, leaving several possible configurations of the investigated molecule within a three dimensional space.1,2

To overcome this limitation we applied a second measurement technique, probing the permanent dipole moment and thus giving information of a second axis within the molecular frame. This method itself already allows for a prediction of the dye alignment. Further, if combined with the optical measurements, the properties of two molecular axes can be deduced.1,2

We applied this novel method to two well-known Ir-complexes, fac-tris(2-phenylpyridine)iridium(III) (Ir(ppy)3)and its heteroleptic counterpart Bis(2-phenylpyridino)acetylacetone)iridium(III) (Ir(ppy)2(acac)). The orientation of the emissive transition dipole moment of both molecules has been determined several times,
revealing the preferential alignment of the Ir(ppy)(acac) molecule, while the homoleptic compound showed isotropic behavior.[4] Nevertheless, the only predictions of the molecular alignment made so far, rely on computational methods such as molecular dynamics simulations. [9]

After carefully taking the amorphous nature of organic guest host systems into account, the application of the combined method revealed the preferential alignment of the heteroleptic compound, which is in agreement with earlier predictions. Furthermore the homoleptic dye molecule was confirmed to be isotropically oriented within a certain threshold of measurement uncertainty.

The application of this novel technique is not only limited to transition metal complexes in organic guest-host systems but can also be applied to any polar film within organic optoelectronic devices.


SYMPOSIUM EP02

Photonic Materials and Devices for Biointerfaces
April 23 - April 25, 2019

Symposium Organizers
Anthony Banks, NeuroLux
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Xiaoting Jia, Virginia Institute of Technology
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* Invited Paper

SESSION EP02.01: Photonic Materials and Devices for Biointerfaces I
Session Chairs: Xiaoting Jia and Xing Sheng
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 223

10:30 AM *EP02.01.01
Combined Optoelectronics and Transparent Electronics for Neural Imaging and Optogenetics Applications Zhongping Ma; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Flexible electronics which can be bent, folded and/or stretched, have been applied to various applications, such as biomedical implants and wearable devices, due to their thin structure to facilitate less invasive clinical operations. Flexible devices combined with optoelectronic systems extend to a range of applications such as biomedical stimulations and recordings using light sources, especially as optogenetics. Because light is the primary stimulation tool for optogenetics, optoelectronics benefit from using transparent devices by precisely matched exposing light on the recording site through transparent electrodes. Recently, many research studies have shown that graphene is an excellent candidate as a recording electrode due to its excellent electrical/thermal conductivity, transferability, and mechanical properties. Furthermore, the biocompatibility and broad-wavelength transparency from the ultraviolet (UV) to the infrared radiation (IR) spectrum of graphene make it ideal for the replacement of metal counterparts in optogenetics stimulations, recordings, and imaging applications. Our preliminary results indicate a viable approach combining a hybrid optoelectrical system with light emitting diodes (LEDs) and graphene to fabricate an implantable optogenetics system capable of simultaneous stimulation and recording. However, in our previous work, a laser was used as the light source for neural stimulation externally. Graphene devices without an internally mounted light source are not capable of operating under fully implanted condition. In this work, we built a multifunctional implantable system utilizing nitride-based microscale light emitting diodes (LEDs) vertically stacked on top of graphene electrodes through which light can pass through, enabling synchronous stimulation and recording on an electrocorticogram (ECoG) system utilizing transparent graphene. As such, this study demonstrates graphene electrodes integrated with high-performance flexible optoelectronics devices in thin-film and flexible platform has unique applications in multifunctional optogenetics systems for various clinical operations. Prospective studies will examine the effects and impact of hybrid optoelectronics on the surface of the animal tissue and performing simple animal behavioral experiments. Acknowledgment: The work was supported by ARO (W911NF-14-1-0652) and partly by DARPA (N66001-17-2-4010).

11:00 AM *EP02.01.02
Soft Electronic Implants Based on Ultrathin Image Sensors and Biodegradable Drug Delivery Devices De-Hyeyong Kim2, 1; 1Seoul National University, Seoul, Korea (the Republic of); 2Institute for Basic Science, Seoul, Korea (the Republic of).

Although recent efforts in materials development, device designs, and fabrication strategies have resulted in meaningful progresses to the goal of high performance soft implantable bioelectronics, significant challenges still remain. In the first part of this presentation, we report our recent achievement in a ultrathin high-density curved image sensor (CurvIS) array for soft retinal prosthesis. The ultrathin image sensors use a heterostructure of inherently soft 2D materials (MoS2 and graphene) and employ ultrathin and strain-isolating array designs for the human-eye-inspired hemispherically curved design. This high-density soft CurvIS array with the single-lens optics successfully acquires pixelated images without optical aberration and infrared noises, whose potential for application to soft subretinal prosthesis was proved through the animal experiment. We then briefly report the recent achievement in the biodegradable drug delivery device for brain tumor treatment. The integration of wireless sensing and actuation function to the biodegradable drug delivery device enables high therapeutic efficacy with long term biocompatibility.

11:30 AM EP02.01.03
Evaluation of Durability of Transparent Graphene Electrodes for Chronic In Vivo Experiments David Ding, Ruoyu Zhao, Xin Liu, Yichen Lu, Ryoma Hattori, Chi Ren, Takaki Koniyama and Duygu Kuzum; University of California, San Diego, La Jolla, California, United States.

Long-term in vivo multimodal studies combining 2-photon microscopy, optogenetics and electrophysiology are essential for investigating functions of neuronal circuits with high resolution and precision. Graphene is a unique neural interface material enabling cross-talk free integration of electrical and optical recording and stimulation techniques in the same experiment. In addition to optical transparency, graphene also offers other desirable properties such as ultra-flexibility, high conductivity and biocompatibility. To date, graphene-based microelectrode arrays have been demonstrated in various multi-modal acute experiments involving electrophysiological sensing or stimulation, optical imaging...
and optogenetics stimulation [1-3]. However, understanding chronic reliability of graphene-based transparent interfaces is very important to expand the use of this technology for long-term behavioral studies with animal models. In this work, we investigate chronic durability of transparent graphene electrodes fabricated on polyethylene terephthalate (PET) and SU-8 substrates using in vitro accelerated aging tests. We present our results on simultaneous 2-photon imaging and electrical recording in chronically implanted transgenic mice over the course of two months.

References:

11:45 AM EP02.01.04
Enokitake-Like Vertically Aligned Gold Nanowires for Highly Stretchable Electronics
Shu Gong, Yan Wang and Wenlong Cheng; Monash University, Clayton, Victoria, Australia.

One of the most important mission in wearable electronics is to devise thin, soft, stretchable electronics to circumvent fundamental limitation between soft tissues and rigid electronics. However, progress is hampered by non-trivial engineering, materials, biological, energy systems and data science challenges. The most fundamental of these is failure of the soft/rigid material interface due to mismatching Young’s moduli, which limits stretchability and durability of current systems. At the same time, wearable electronic devices are required to be highly biocompatible without fouling and immune responses. Ultimately, they could become parts of our organs, enabling true remote biodiagnostics anytime and anywhere.

One-dimensional (1D) nanomaterials should be a pathway to achieve these unique features simultaneously, owing to their intrinsically high aspect-ratio that enables the construction of conductive percolation network with small amount of material usage while maintaining high optoelectronic performance. Moreover, 1D nanomaterials have better mechanical elasticity than corresponding bulk materials or sphere-like nanoparticles and this is a key requirement for designing electronic skin materials by circumventing material delamination and/or cracking. Here we show that standing enokitake-like gold-nanowire-based films chemically bonded to an elastomer can be stretched up to 900% and are highly durable, with >95% conductivity recovery even after 2000 stretching/releasing cycles to 800% strain. This is attributed to standing enokitake-like nanowire structures, vertically aligned configuration, and strong chemical bonding interactions between standing nanowire films and elastomeric substrates. Consequently, our gold nanowire thin film offers an effective and appealing platform for highly stretchable multifunctional electronic skin system including stretchable interconnects, location- and sharpness-specific sensors, stretchable transistors and energy devices. We believe our technology showed great promise for future wearable and skin-conformal electronics in bio-monitoring and soft robotic applications.

1:30 PM *EP02.02.01/EP03.02.01/EP04.02.01
Skin-Inspired Organic Electronics
Zhenan Bao; Stanford University, Stanford, California, United States.

Flexible organic electronics have attracted considerable attention over the past decade. Stretchable electronics represent another type of optoelectronic devices that are intrinsically elastic, that is they are foldable, twistable, and stretchable while maintaining performance, integrity and durability. Incorporated into devices, properly designed stretchable materials may result in more robust devices under bending and strain compared to flexible but not stretchable materials. For intrinsically stretchable electronics, it is desirable to have intrinsically stretchable materials, ranging from stretchable conductors, stretchable dielectric to stretchable semiconductors. In this talk, I will present various molecular design concepts for realizing stretchable electronic polymers without compromising electronic properties. Their applications in bioelectronics will also be presented.

2:00 PM *EP02.02.02/EP03.02.02/EP04.02.02
Flexible Bioelectronics—Enzyme-Based Body-Worn Electronic Devices
Joseph Wang; University of California, San Diego, La Jolla, California, United States.

Wearable bioelectronic devices rely on oxidoreductase enzymes and have already demonstrated considerable promise for on-body applications ranging from highly selective non-invasive biomarker monitoring to epidermal energy harvesting. Critical to such progress is the judicious design of the enzyme-electronic interface, along with flexible platforms with mechanical properties similar to those of biological tissues. Such devices require special attention to the enzyme-electronic interface and to several considerations related to wearable applications, such as mechanical properties (flexibility and stretchability), operational stability in different biofluids and under changing conditions (e.g., pH, temperature), biofouling, selectivity, and low target concentrations. Keeping these requirements in mind, our group has pioneered a variety of wearable biocatalytic sensors and biofuel cells devices. By leveraging the advantages of biocatalysis, electrochemistry, and flexible electronics, and addressing key challenges, wearable bioelectronic devices could have a tremendous impact on diverse biomedical, defense and defense fields.

2:30 PM EP02.03/EP03.02.03/EP04.02.03
Human Skin Interactive Bio-e-skin for Self-Powered Health Care Monitoring
Dipankar Mandal, 1, 2 and Sujoy K. Ghosh; 1 Institute of Nano Science and Technology, Mohali, India; 2 Department of Physics, Jadavpur University, India, India.

Among various pressure sensors, transduction mechanisms, piezoresistive, capacitive, triboelectric, and piezoelectric effects are generally considered for converting tactile stimuli into electrical signals. 1, 2 Owing to the fast response time and higher sensitivity, piezoelectric pressure sensors (PEPS) are the most useful for the detection of full-range human activities. It has been found that pressure sensor based artificial electronic skin (e-skin) can mimic the human skin and detects subtle pressure (1 Pa–1 kPa). A broad range of applications is expected to be implemented such as wearable health care systems, human–machine interfacing devices, artificial intelligence and prosthetic skin. Nevertheless, piezoelectric materials with adequate flexibility, high weight, ease of large-area processing, low cost and environmental safety are attractive but several issues are remaining for next-generation pressure/sforce sensors and mechanical energy harvesters. Recent advances on PEPS development is primarily focused on varies types of inorganic and semiconducting piezoelectric materials such as, barium titanate (BaTiO3), zinc oxide (ZnO), zinc sulfide (ZnS) and lead zirconate titanate (PZT). 3 In spite of their superior electromechnical responses, the brittleness and toxic properties limit their implementation in wide range of biomedical and flexible electronics applications. On the other hand, natural piezoelectric materials are not yet extensively investigated as an e-skin for measuring and quantifying human physiological signals. 2 In this context, we have developed human skin interactive self-powered piezoelectric biomaterials based e-skin (Bio-e-skin) which can detect and discriminate acute human physiological signals such as low frequency as subtle as wrist pulse and even intra-body pressures such as intracranial and intracardinal pressure, to relatively high frequency dynamic human motions such as movements of synovial joints of wrist, elbow, knee and finger bending. Natural bio-polymers such as, collagen, chitin, gelatin and cellulose were found to possesses superior mechanosensitivity which was sufficient to fabricate self-powered wearable bio-e-skin that can mimic spatiotemporal human perception and monitors real-time human physiological signals in non-invasive rational strategy. In addition, the bio-skins are found to generate superior output power density which is sufficient to operate the commercial consumer electronics. These observations suggest that fabricated bio-e-skins could eventually find a wide range of applications in autonomous epidermal
electronics, implantable medical device, surgery, e-healthcare monitoring, in vitro and in vivo diagnostics apart from its broad range applications in the field of self-powered personal portable electronic devices.3–5

References

2:45 PM *EP02.02.04/EP03.02.04/EP04.02.04
Fully Implantable Wireless Battery-Free Optoelectronic Systems for Multimodal Optogenetic Neuromodulation
Philippe Gaturol, Vaidhnavi Krishnaanarthi, Abraham Vázquez-Guadado, Zhaoqian Xu, Anthony Banks, Chun-Ju Su, Yeshou Xu, Chad Haun, Emily A. Waters, Irawati Mandela, Siddharth Krishnan, Tyler Ray4, John P. Leshock4, Yonggang Huang4, Debasish Chanda1 and John A. Rogers4; 1University of Arizona, Tucson, Arizona, United States; 2RMIT University, Melbourne, Victoria, Australia; 3University of Central Florida, Orlando, Florida, United States; 4Northwestern University, Evanston, Illinois, United States; 5NeuroX, Evanston, Illinois, United States.

Recently emerging classes of battery free, ultrasmall1, fully implantable devices for optogenetic neuromodulation2 eliminate physical tethers associated with bulky head-stages and batteries in alternative wireless technologies and conventional setups by leveraging cellular scale light emitting diodes on flexible implantable light sources3. These highly miniaturized systems enable untethered, operation for behavioral studies that eliminate motion constraints and enable new experimental paradigms in a range of complex 3D environments and contexts (e.g. social interactions) that cannot be explored with conventional technologies. These devices are, however, purely passive in their design, thereby precluding any form of active control or programmability, resulting in limitations when investigating circuit dynamics where independent operation of multiple light sources with precise active control is needed. Here we present a series of important concepts that enable controlled device operation, independent of position and angle relative to the experimental arena, with advanced wireless power harvesting capabilities and full user-programmability over multiple devices. This level of functionality is demonstrated in integrated platforms that are compatible with noninvasive imaging technologies such as computed tomography and magnetic resonance imaging and have sizes and weights not significantly larger than those of previous, passive systems. The resulting devices qualitatively expand options in brain tissue illumination for optogenetic neuromodulation and multimodal operation, with broad potential applications in neuroscience research, with specific advances in precise dissection of neural circuit function during unconstrained behavioral studies.


3:00 PM BREAK

3:30 PM *EP02.02.05/EP03.02.05/EP04.02.05
Self-Powered Ultra-Flexible Organic Electronics for Health Monitoring Takao Someya1, 2, Kenjiro Fukuda2 and Tomoyuki Yokot3; 1Electrical and Electronic Information Systems, University of Tokyo, Tokyo, Japan; 2RIKEN Center for Emergent Matter Science, Saitama, Japan.

On-skin sensors have attracted much attention as the next-generation wearable devices, because the conformal contact on human skin enables accurate and continuous detection of physiological signals. One of the most important technologies to improve usability of on-skin sensors is a power source to continuously supply electricity to health-monitoring systems. In this talk, we will report on recent progresses of ultraflexible organic photovoltaic cells for applications to wearable sensors. First, ultraflexible organic power sources that can be wrapped around an object have been developed with mechanical and thermal stability in long-term operation. Then, the integration of these power sources with functional electric devices including sensors has been achieved.

4:00 PM *EP02.02.06/EP03.02.06/EP04.02.06
Physical Biology and Material Dynamics at the Semiconductor-Based Biointerfaces Bozhi Tian; The University of Chicago, Chicago, Illinois, United States.

Recent studies have demonstrated that in addition to biochemical and genetic interactions, cellular systems also respond to biophysical cues, such as electrical, thermal, and mechanical signals. However, we only have limited tools that can introduce localized physical stimuli and/or sense cellular responses with high spatiotemporal resolution. Inorganic semiconductors display a spectrum of physical properties and offer the possibility of numerous device applications. My group integrates material science with biophysics to study several semiconductor-based biointerfaces. In this talk, I will first pinpoint domains where semiconductor properties can be leveraged for biointerface studies, providing a sample of numbers in semiconductor-based biointerfaces. Next, I will present a few recent studies from our lab and highlight key biophysical mechanisms underlying the non-genetic optical modulation interfaces. In particular, I will present a biology-guided two-step design principle for establishing tight intra-, inter-, and extracellular silicon-based interfaces in which silicon and the biological targets have matched mechanical properties and efficient signal transduction. Finally, I will discuss new materials and biological targets that could catalyze future advances.

4:30 PM *EP02.02.07/EP03.02.07/EP04.02.07
Autonomic Self-Healing and Intrinsical Stretchability of PEDOT:PSS Films Fabio Cicoira; Chemical Engineering, Polytechnique Montréal, Montréal, Quebec, Canada.

Organic electronic devices, apart from consumer applications, are presently paving the path for key applications at the interface between electronics and biology. In such applications, organic polymers are very attractive candidates, due to their distinct properties of mechanical flexibility, self-healing and mixed conduction. Major group investigated the processing conditions leading to high electrical conductivity, long-term stability in aqueous media as well as robust mechanical properties of the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS) [1-3]. We have demonstrated that stretchable PEDOT:PSS films can be achieved by adding a fluorosurfactant to the film processing mixture and by pre-stretching the substrate during film deposition. We have achieved patterning of organic materials on a wide range of substrates, using orthogonal lithography and pattern transfer [4-5]. Recently we have discovered that PEDOT:PSS films can be rapidly healed with water drops after being damaged with a sharp blade [6] or show autonomous self-healing if processed in presence of certain additives. My talk will deal with processing, characterization and patterning of conducting polymer films and devices for stretchable, stretchable and healable electronics. I will particularly focus on the strategies to achieve films with optimized electrical conductivity and mechanical properties, on unconventional micro patterning on stretchable substrates, on the different routes to achieve films stretchability and self-healing.

F. Cicoira et al. APL Mat.3, 014911, 2015.

4:45 PM *EP02.02.08/EP03.02.08/EP04.02.08
Implantable Neurotransmitter Monitoring Based on Luminescent MOFs and Flexible Electronics Hang Xu, Wei Ling and Xian Huang; Department of Biomedical Engineering, Tianjin University, Tianjin, China.
In this work, Nd3+ high temperature (400°C) with high external pressure (200 bar), allows for the elaboration of luminescent GSAG:Nd NPs with an average size of 80 nm [3,4]. The liquid-based property (MRI contrast), defining GSAG:Nd NPs as multifunctional nanoprobes. (NPs) are promising candidates for chemical stability and intrinsic luminescence in the near infrared (NIR) region, overlapping with the biological optical transparency window, rare-earth doped oxide nanoparticles are used for all-optical control of cell behaviour [3].

Beyond these unique lasers, my lab develops an implantable high-resolution light source for advanced optogenetics studies. Again, miniaturization of photonic devices to sub-cellular dimensions is the key challenge. Organic light-emitting diodes (OLEDs) are highly attractive in this context, in particular due to their low toxicity, mechanical flexibility, high brightness, and ability to provide patterned illumination at very high spatial resolution. OLED microarrays containing >100,000 individual OLED pixels with µm dimensions are used for all-optical control of cell behaviour [3].

I will present our work on new micro- and nano-photonic devices for studying cell biology and small animals. Our lab is most well-known for the Guinness World Record invention of the biological laser [1]. By inserting sub-µm sized lasers into live cells, we tag and track individual cells in large cell populations and over extended periods of time [2]. We are currently developing this further to perform in vivo intracellular sensing and cell tracking, e.g. in the heart of zebras.

The optofluidic bio-laser is an emerging technology in biosensing and imaging. In contrast to traditional fluorescence based measurement, lasing emission is used as the sensing signal, which has strong intensity, threshold behavior, and narrow linewidth, and is free of background. In this presentation, I will first discuss the principle of optofluidic bio-lasers. Then I will discuss three applications with bio-lasers: (1) cellular analysis using cell laser array; (2) intra-cellular laser probes; (3) tissue analysis for cancer diagnosis; (4) neural network monitoring; and (5) ultrasound modulated lasers.

Nanoscale Thermal Sensors Based on Nd3+ Doped GdSc2Al12O19: Luminescent Nanoparticles

Alexandra Cantarano1, Marija Matulionyte2, Alain Ibanez2, Fiorenzo Vetrone2 and Geraldine Dantelle1, 1Institut Néel, CNRS, Grenoble, France; 2Energie Matériaux Télécommunications, INRS, Varennes, Quebec, Canada.

Accurate and non-invasive techniques as well as temperature measurements at the nanoscale have widely spread out with the major development of nanotechnologies and, more specifically, of nanomedicine [1]. Luminescent nanoprobes (quantum dots, dyes, fluorescent polymers, rare-earth doped nanoparticles, etc) have ever since competed to ensure the best thermal sensitivity in the 20 to 50°C temperature range, as well as high bio-compatibility and appropriate size (below 100 nm) for in vivo applications. Due to their high chemical stability and intrinsic luminescence in the near infrared (NIR) region, overlapping with the biological optical transparency window, rare-earth doped oxide nanoparticles (NPs) are promising candidates for in vivo nanothermometry [2].

In this work, Nd3+ doped GdSc2Al12O19: (GSAG:Nd) NPs are investigated as luminescent nanothermometers. The development of a new solvothermal synthesis method, combining high temperature (400°C) with high external pressure (200 bar), allows for the elaboration of luminescent GSAG:Nd NPs with an average size of 80 nm [3,4]. The liquid-based solvothermal reaction induces the adsorption of hydroxyl and alcohlic molecules onto the NP surface, leading to the stabilisation of GSAG:Nd NPs in water. Typical Nd3+ emission was observed under a 808-nm excitation, with two emission bands centred at 938 and 945 nm, corresponding to the electronic 4I13/2 -> 4I9/2 transition split by the crystal field effect. Thermal sensing properties of Nd3+ doped GSAG NPs were found to be excellent for contactless NIR temperature measurements with even higher relative thermal sensitivity as compared to the conventional Nd3+ doped Y3Al5O12 (YAG:Nd) NPs [5]. Additionally, the presence of Gd3+ ions in the GSAG structure offers a further property (MRI contrast), defining GSAG:Nd NPs as multifunctional nanoprobes.


8:30 AM EP02.03.01 Laser-Emission Based Microscopy for Cell, Tissue and Neural Network Analysis

Xudong S. Fan; Biomedical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Given the above consideration, this paper presents techniques and materials to fabricate a luminescent MOF-based flexible sensor, and photoelectric detector in the sensor can detect emission changes of MOF represented as functional part in response to DA. Notably, MOF-modified sensor possesses excellent biologically safety that was confirmed using in vivo cell experiments, supplying the foundation for the practical application in living animals. This work represents the first effort in combing luminescent MOFs with flexible sensors, offering in-depth understanding of flexible sensors’ property at molecular level. The excellent results may promote the progress of flexible electronics in biology, healthcare and sensing, etc.

8:00 AM EP02.03.02 Nanolasers Inside Living Cells and Other Photonics for Bioimplants

Malte C. Gather; School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.

The aim of this work is the synthesis, optimization and functionalization of organic@inorganic core-shell nanoparticles (NPs), which constitute a novel class of tracers, to be used for deep tissue imaging through two-photon fluorescence microscopy of tumor vascularization. These core-shell NPs, which comprise an organic dye nanocrystal core (ca 40-50 nm) surrounded by a silicate shell, are synthesized using an original ‘spray-drying’ method: atomization of the initial sol-gel solutions followed by the drying of the resulting spray in a horizontal furnace, at 150-200°C, under laminar inert gas flow [1]. This one-step synthesis is made possible thanks to the control of both the sol-gel chemistry (hydrolysis and polycondensation of silicon alkoxides used as shell precursors) and the confined nucleation and growth of the organic core, which occur simultaneously, by tuning the physical parameters of the spray-drying reactor: temperature of the furnace and electrostatic filter, gas flow and atomization parameters. Alkoxide precursors, TMOS (tetramethoxysilane)
and TMSE (1,2-bis(trimethoxysilyl)ethane) were particularly selected to form the organosilicate shell. Additionally, an organosilane, (3-azidopropyl) triethoxysilane (AzPTES), is used to impart an azide functionality to the NPs for further functionalization with azide-modified moieties using the Cu(I)-catalyzed 1,3-dipolar cycloaddition of organic azides to azides (CuAAC). The organic dyes for the nanocrystalline core are non-commercial and designed to exhibit high fluorescence intensity in the crystal-state under two-photon excitation in the red and near infrared (biological window) and the appropriate physico-chemical properties to enable their nanocrystalization [2]. The obtained core-shell NPs feature a very high organic loading (around 30-40%/wt). These very high dye concentration is an important advantage of these core-shell NPs to impart strong brightness by enhancing absorption and emission cross sections through the high number of fluorescent molecules. Thus, NPs suspensions showed intense fluorescence emissions around 600 nm. The NPs were then functionalized with different forms of azide-modified polyethylene glycol (PEG), differing in chain length and structure using CuAAC to render them furtive and increase their circulation time in the bloodstream of mice [3]. The effects of the NP functionalization and colloidal stability were studied using different characterization tools such as IR and fluorescence spectroscopies, dynamic light scattering and zeta potential under physiological conditions. First in vivo tests of two-photon fluorescence imaging in mice showed bright emissions of these new fluorescent tracers with good circulation time higher than 20 min, while fluorescence was still faintly visible in the blood flow even after a day. These preliminary results are promising for vascular and deep-tissue imaging, particularly for angiography to study for example angiogenesis mechanisms in cancer tumors and associated therapeutic treatments.

References

10:00 AM BREAK
10:30 AM EP02.03.05
Semiconductor Laser Particles for Biomedical Applications Seek-Hyun Andy Yun; Wellman Center for Photomedicine and Harvard Medical School, Harvard Medical School, Cambridge, Massachusetts, United States.

Laser particles with sizes of optical wavelengths that are injectable and implantable into biological systems are new, promising light sources and probes for biomedical applications. We present biocompatible semiconductor micro-laser particles for tagging and tracking many cells.

11:00 AM EP02.03.06
Photoluminescence Spectra in ZnO Microspheres—The Interplay of Whispering Gallery Modes and Purcell Effect Ching-Hang Chien1, Bui Trong Huynh Ngo1, 2 and Yin-Chung Chang1, 4. Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan; 1Electrical Engineering, University of Alberta, Edmonton, Alberta, Canada.

Both theoretical and experimental studies of photoluminescence of ZnO microspheres and examine the Purcell effect on spontaneous and stimulated emission related to whispering gallery modes are presented. A Mie-basis Green function method, which incorporates contributions from leaky modes, spontaneous as well as stimulated emission processes, and Purcell effect is presented. We show that the spontaneous emission spectrum calculated according to Mie theory (without the Purcell effect) is related only to the contribution of leaky modes, while the spontaneous and stimulated emission both enhanced by the Purcell effect are responsible for the main WGM resonance peaks observed experimentally. It is found that the stimulated emission peaks are doubly enhanced by their respective mode quality factor Q: one factor from the Purcell effect and the other factor from the photon density derived from the rate equation. After taking into account this double enhancement in stimulated emission, the Purcell effect on spontaneous emission, and the leaky-mode contributions, the theory can provide a quantitative description of the detailed fine features of both TE and TM modes observed in the photoluminescence spectra in the whole visible region of ZnO microspheres with various degrees of porosity. The quantitative understanding of the interplay of these emission mechanisms should prove useful for optimizing the performance of light-emitting devices based on micro resonators.

11:15 AM EP02.03.07
Precise Ultrasound-Cell Biointerface Mediated by Fiber-Based Photoacoustic Converter with Controllable Frequency Linli Shi and Chen Yang; Boston University, Boston, Massachusetts, United States.

Ultrasound technique arouses great interests in biomedical and clinical application since it holds promise in noninvasive therapeutic studies. Thus, the ultrasound-cell biointerface for drug delivery, neuron stimulation and gene transfection attracted great attention. However, the insufficient resolution and the large device size of current ultrasound technology limit its applications. In this work, we developed a miniaturized optical fiber-based photoacoustic converter. The converter is with a diameter of ~500 microns to 1 millimeter and composed of nanoparticle-polymer material to produce localized acoustic wave with controllable frequency in a biomedical relevant range of 0.2-1.9 MHz. A coating scheme with a diffusion layer and expansion layer was designed on the tip of the fiber converter. The inverse proportionality between the diffraction layer thickness and the peak frequency was observed. Meanwhile, the light penetration depth of the absorption/thermal expansion layer also exhibited similar inverse proportionality to the peak frequency, offering two approaches toward controllable frequency. Moreover, the acoustic frequency spectrum shows narrow bandwidth (Full width at half maximum FWHM <2.5 MHz), high angular stability as well as a longitudinal penetration depth of 12 cm in chicken breast, enabling a level of precise control for biomedical ultrasound application. Importantly we demonstrated localized neuron stimulation in vitro and in vivo utilizing the optical photoacoustic converter. Based on these results, the new miniaturized fiber optoacoustic converter exhibits capability for in-depth study about the biointerface between localized acoustic with tunable frequency and specific cells, benefitting further research and clinical study for imaging, molecule delivery and other therapeutic applications.

11:30 AM EP02.03.08
Direct Laser Writing of Silk Fibroin Optical Waveguides Molilia Santos, Sabrina Santos, Renato Martins, Juliana Almeida, Kelly Paula, Gustavo Almeida, Sidney Ribeiro and Cleber Mendonca; State University of Sao Paulo, Sao Carlos, Brazil.

Silk fibroin is an abundant natural polymer, which in the last years has been studied as an attractive high-technology material platform, offering new opportunities for photonics and optoelectronics applications. In the field of photonics, silk fibroin-based films have been identified as an interesting optical material due to its transparency from the visible to the near infrared, favoring the development of several devices, such as photonic crystals, diffraction gratings and waveguides. Concomitantly, femtosecond laser direct writing (fs-DLW) has proven to be an important method for materials processing, enabling the fabrication of optical devices in a wide variety of materials, being useful for the obtaining of optical waveguides, microfluidic channels, and 3D flexible electronic circuits. One of the main advantages of fs-DLW is the reduction of thermal effects, which is of foremost importance for processing biomaterials. In spite of that, the usage of femtosecond laser to produce optical elements in silk fibroin has not been demonstrated yet. Therefore, in this work we demonstrate the ability to write optical waveguides in silk fibroin using fs-DLW. Homogeneous, 10-mm long waveguides were fabricated by irradiating a 42-µm thick silk fibroin film with femtosecond pulses, employing a pulse energy of 26 nJ and a scan speed of 100 µm/s. The guiding profile was simulated using the finite element method and experimentally observed by coupling light at 632.8 nm. Such waveguides, having the property of being biocompatible, are promising to be used in the frontier of biophotonics, from implantable medical devices to biosensors.

SESSION EP02.04: Photonic Materials and Devices for Biointerfaces III
Session Chairs: Wenlong Cheng and Xiaoting Jia
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 223

1:30 PM EP02.04.01
Flexible and Stretchable Integrated Photonics Juejuan Hu; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Integrated photonics, which involves a multitude of miniatuized optical components connected by an optical waveguide network on a single substrate, has thrived over the past decades and is now widely regarded as a transformative paradigm shift in optics and photonics analogous to integrated circuits revolutionizing the electronic industry. Integrated photonics platforms demonstrated thus far are predominantly fabricated on rigid substrates. By imparting mechanical flexibility to integrated photonic structures, the technology bodes significant application potential for imaging, sensing, communications, and consumer electronics. Over the past few years, we have developed a suite of active and passive photonic devices and systems integrated on plastic substrates which can be repeatedly bent, twisted, and stretched without damage. This is accomplished through coherent optical/mechanical co-design, which ensures superior mechanical flexibility and ruggedness of the devices while maintaining, and in some cases enhancing their optical performances. In this talk, the design rationale, fabrication protocols as well as strain-optical coupling behavior in these devices will be reviewed, and their applications in biomedical monitoring and high-speed data communications will be discussed.

2:00 PM EP02.04.02 Plasmonic Nanostuctures Modified Multifunctional Fiber for Optical Biochemical Sensing and Electrical Neural Recording Yuimo Zhang, Jungyeob Song, Li Yu, Meitong Nie, Wei Zhou and Xiaoting Jia; Bradley Department of Electrical & Computer Engineering, Virginia Tech, Blacksburg, Virginia, United States.

Plasmonic nanostructured surfaces have received great attention over recent years. The unique optical properties of plasmonic nanostructures enable chemical and biological sensing using refractive index sensing and surface-enhanced Raman scattering (SERS). However, there are few reports about the combination of optical biochemical sensing and electrical neural recording. Here, we present plasmonic nanostucture modified multifunctional fiber probes that allow for both optical biosensing and neural recording. These fibers are fabricated by thermal drawing process and nanostuctured surface modification. We demonstrate the usefulness of this device as a sensitive refractive index sensor as well as SERS substrate. Also, neural recording in wild-type mice confirms that our probes can be used for electrical interrogation of neural circuits in vivo. Technology developed here can be potentially used for in situ in vivo optical biochemical sensing and electrical neural recording.

2:15 PM EP02.04.03 Bioconjugated Semiconductor Polymer Nanotransducers for Minimally Invasive Optoacoustic Neurostimulation Yimin Huang1, Ying Jiang1, Jiayingzi Wu1, Ji-Xin Cheng2 and Chen Yang3; 1Boston University, Boston, Massachusetts, United States; 2Purdue University, West Lafayette, Indiana, United States.

Neuromodulation has been an invaluable approach for treating neurological diseases. Optogenetics has been developed as a powerful method that is capable of modulating neural activity in rodents. However, application of optogenetics in humans is limited due to its requirement of viral infection. Recently, nanostructures showed great promise for modulating neuronal activities through a minimally invasive manner. Yet, the local temperature rise induced by the thermal effects of nanostructures impose a fundamental challenge for neuromodulation under physiological condition. To address these challenges, we developed an optoacoustic neuro-stimulation platform via semiconducting polymer nanotransducers (SPN) that efficiently convert pulsed laser energy into acoustic waves to enable highly localized stimulation of a neural tissue. Here, we demonstrated that the designed SPNs can strongly absorb light in the near-infrared second window (NIR-II, 1030nm), enabling enhanced light penetration depth through the skull. We further bioconjugated the surface of SPNs with antibodies targeting mecano-sensitive channels, TRPV4, to specifically bind to the neural membrane within 1 hour. By locally perturbing the mechano-sensitive channel, SPN can trigger repeatable action potential firing of embryonic cortical neurons with a laser duration of 3 ms. With enhanced temporal and subcellular spatial resolution, the as-designed SPNs showed potential in precise control of the neuronal circuits in the brain for basic neuroscience studies and treatment of neurological disorder diseases.

2:30 PM BREAK

3:30 PM *EP02.04.04 Monocrystalline Silicon Nanomembrane Micro- and Nano- Structures for Bioreosorbable Optical Sensors Weidong Zhou1, Zhonghe Liu1, Jiho Shin2, Wuhin Bai2, Yonghao Liu2, Yuze A. Sun2 and John A. Rogers1,3; 1Department of Electrical Engineering, The University of Texas at Arlington, Arlington, Texas, United States; 2Department of Chemical and Biomolecular Engineering, University of Illinois at Champaign-Urbana, Urbana, Illinois, United States; 3Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; 4Center for Bio-Integrated Electronics, Northwestern University, Evanston, Illinois, United States.

We report here monocrystalline silicon nanomembrane based optical waveguides, photonic crystals, and Fabry-Perot cavities for bioreosorbable sensors. Both micro- and nano-scale structures have been designed, fabricated, and characterized for gas, liquid, pressure, temperature, and other physiological parameter monitoring.

4:00 PM *EP02.04.05 Stretchable Microscale Surface-Emitting Lasers as a Patternable Coherent Light Source for Biointegrated Optoelectronics Jongseung Yoon; Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States.

Vertical cavity surface emitting lasers (VCSELs) represent a ubiquitous coherent light source that can provide unique performance characteristics superior to those possible with edge-emitting lasers or light-emitting diodes. Despite such compelling advantages, existing VCSEL technologies rely on millimeter scale dies produced by wafer-sawing, robotic pick-and-place, and wire bonding, thereby imposing fundamental limitations on the device size, spatial density, level of power, choice of substrate materials, and efficiency of materials utilization. Furthermore, VCSELs, built on rigid and brittle semiconductor wafers, intrinsically restricted their conformal, bio-compatible integration onto soft, curvilinear surfaces of biological systems. This talk will provide an overview of recent advances in materials design and fabrication strategies of printable microscale VCSELs (micro-VCSELs) capable of overcoming above-described limitations and providing new capabilities in various unconventional areas of applications including flexible laser displays, flexible optofluidic sensors, and skin-conformal blood flow sensors.

4:30 PM EP02.04.06 Metal Oxide in Photovoltaic BioInterfaces Enables Capacitative Photostimulation of Neurons Shashi B. Srivastava1, Rustamzhon Melikov1, Ugur M. Dikbas1, Ibrahim H. Kavakali1-4 and Sedat Nizamoglu1-2; 1Electrical and Electronics Engineering, Koc University, Sariyer, Turkey; 2Graduate School of Biomedical Sciences and Engineering, Koc University, Sariyer, Turkey; 3Department of Molecular Biology and Genetics, College of Science, Koc University, Sariyer, Turkey; 4College of Engineering, Chemical and Biological Engineering, Koc University, Sariyer, Turkey.

Development of safe and efficacious neural interfaces is important for the treatment of a broad range of neural diseases such as Alzheimer’s disease, restoration of motor activity, and blindness due to retinal degeneration [1]. Two basic charge transfer mechanisms, Faradaic and capacitive processes, have been widely used for neural interfaces [2,3]. Faradaic charge transfer involves the charge carrier injection in the extracellular medium with chemical reactions, which may generate harmful side products. Alternatively, capacitive charge transfer is originated by the movement of ions via electromagnetic interactions without any reaction. For neural photostimulation, semiconducting polymers have engrossed significant attention due to their easy solution processability, biocompatibility, flexibility and conformability [4], and capacitive photostimulation by organic interfaces offers a safe and long-term neural stimulation strategy. Here, we demonstrate a photodetector architecture that can generate capacitative photostimulation. We use a bulk heterojunction of P3HT(Poly(3-hexylthiophene-2,5-diyl)):PCBM[(6,6)-phenyl-C61-butyric acid methyl ester) for the phototactive layer, which is biocompatible and can stimulate neurons [4, 5]. We explore the phototactive layer on zinc oxide nanoparticles, which is deposited on ITO layer. The photocurrent measurements suggest that the photodetector shows capacitive charge transfer mechanism. Further, electrophysiology experiment using patch pipette in voltage clamp mode is performed on SH-SY5Y neuronal cells and strong depolarization is observed by 10 ms light pulses in the visible range. Moreover, the results are confirmed by theoretical two-domain-stimulation model as well. In perspective, utilization of metal oxide for controlling photostimulation mechanism provides a new opportunity for safe and extended photostimulation of neurons.

References
4:45 PM EP02.04.07
Stain-Resistant Superomniphobic Flexible Optical Plastics Based on Nano-Enoki Mushrooms
Saied Hashanifar and Paul Leu; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

In this paper, we demonstrate the stain-resistance and high-pressure stability of superomniphobic flexible optical plastics. A scalable method for creating nano-enoki mushrooms in plastics is presented that provides for the re-entrant geometry needed to prevent infiltration from a variety of liquids. The surface demonstrates static contact angles over 150° and low contact angle hysteresis under 20° for a wide variety of organic liquids. The re-entrant tops and fluorination of the nano-enoki, as well as the few micron spacing between nanostructures, provide for robust metastable solid-liquid-air interfaces in the presence of Laplace pressures of at least 900 Pa. In addition, compared to the initial bare plastic, the nano-enokis demonstrate comparable transmission values (86.4% versus 88.4% at a wavelength of 550 nm) and ultrahigh haze values (96.4% versus 1.1%). The surfaces exhibit stain-resistance for a variety of liquids including mustard and blood, where dried blood and mustard both flake off the samples without any residue. We also performed durability experiments which demonstrate that nano-enoki plastics are robust from bending with similar transmission, haze, wetting contact angle and hysteresis values after 5000 cycles of bending.

In the presence of incident light, the current between the protruding electrodes is proportional to the photodiode area and light intensity and serves to stimulate nearby neurons. The tuning of this current by the light intensity means that stimulation thresholds need not be known a priori, allowing dynamic in vivo testing. Further, the voltage applied between the electrodes is proportional to the number of photodiodes in series, allowing the applied voltage and electrode spacing to be engineered for a particular specific application. We discuss possible applications for these devices, especially in shallow brain regions such as the rat motor cortex.

Optically-Powered Wireless Electronics for Neural Stimulation
Samantha Norris, Alejandro Cortese, Conrad Smart, Teja Bollu, Michael Reynolds, Yanxin Ji, Jesse Golberg and Paul L. McEuen; Cornell University, Ithaca, New York, United States.

We describe the fabrication and characterization of wireless, implantable devices for the electrical stimulation of neural tissue. The devices consist of silicon photodiodes created by selectively doping the top of the device layer to create a vertical PN junction. The photodiodes are then electrically isolated by dry etching to the underlying oxide layer, and connected in series to drive two metal electrodes on either end of the device. The photodiodes are encapsulated with SU8, leaving the metal electrodes protruding. The devices are releasable into solution using a combination of dry and wet etches, and then can be dried and inserted into tissue using custom microencapsule insertion techniques. The entire process utilizes silicon-on-insulator substrates and traditional photolithographic techniques, which enables the production of these devices and their release from the substrate to be performed in massive parallel.

In recent years, there has been a tremendous advancement in bio-inspired electronic devices. Multiscale structures of biological materials exhibit inherent multifunctional integration. Special properties of biological materials provide motivation to scientists and engineers to design highly efficient electronic devices. Inspired by this, we used a protein photosystem I to make efficient photovoltaic solar cells. Photosystem I (PSI, ~500 kDa protein super complex) has been widely used to efficiently capture sunlight, which can create efficient biohybrid photon energy conversion devices. During photosynthesis, photoexcited electrons are transported at a 1 μs time scale across the thylakoid membrane by using PSI as a photodiode at a quantum efficiency closing to 100%. Since PSI photosystem I protein has light induced property, it can be utilized to convert solar energy to electrical energy in Photovoltaic devices. We used this light inducing property of PSI and made biohybrid photovoltaic solar cell using gold surface. Biohybrid photovoltaic solar cell provides novel results on the relationship between surface plasmon generation (SPG) efficiency of nanoslit and the experimentally obtained photocurrent generation, by immobilizing PSI on gold nanoslit electrode surfaces. Semi-analytical reduced calculations were used to calculate SPG (Surface Plasmon Generation) efficiency for varying nanoslits (50 nm, 100 nm, 200 nm, 300 nm or 400 nm). FDTD (finite difference time domain) simulation was also done to find which nanoslits have maximum electromagnetic field enhancement around their surface. Different Nanoslits (50nm, 100 nm, 200 nm, 300 nm or 400 nm) were fabricated with the help of photolithography technique and FIB (focused ion beam). After that, the PSI protein was immobilized on the Nanoslits with the help of self-assembly monolayer formation, and photocurrent generation for each nanoslits was measured using electrochemistry setup. The results show the relationship between SPG efficiency of nanoslits and experimentally obtained photocurrent generation, by immobilizing PSI on the gold nanoslit electrode surface. The photocurrent generation (G) and SPG efficiency for the nanoslit electrochemical devices (D) is a function of nanoslit width. The energy conversion (photocurrent) is greatly enhanced, which is correlated to the SPG efficiency and EM field enhancement in the nanoslit. This finding can be attributed to the phenomenon of plasmon-exciton coupling effect on the PSI in the nanoslits. The enhanced photocurrent generation was explained on the basis of plasmonic light trapping and plasmon-induced resonance energy transfer.

Lightfast and Mechanically Stable Black Coatings on Aluminum Based on Bio-Inspired Structurally Colored Porous Anodic Alumina Layers
Mikhail Pashchanka and Jörg J. Schneider; Technical Univ-Darmstadt, Darmstadt, Germany.

Optical and photonic properties of porous anodic alumina (PAA) layers have gained considerable attention of late.[1] Although pure alumina is known to be a reflective, transparent and intrinsically colorless insulating material, the absorption of light of certain wavelengths can be achieved in PAA due to photonic effects and destructive interference.[2] It is known from previous studies that there is a correlation between such parameters as the pore size and inter-pore distance and the nominal wavelength of the maximal destructive interference, and consequently also observable optical characteristics. Therefore, PAA with different introduced degree of disorder should demonstrate the absorption in a larger wavelengths interval. Black coloring of PAA films is frequently observed when the phenomenon called “burning” (that is a strong increase of the electrical current, accompanied by local etching and distortion of the ordered structure) occurs during the electrochemical synthesis.[3] However, the nature of this coloring remains relatively unexplored.

Here, we demonstrate that the black coloration mechanism in PAA is identical to the one that already exists in natural structurally colored surfaces, or in some artificially created biomimetic structures (similar to the ‘moth eye effect’ or the coloration of the pied paddy skimmer dragonfly wings surface). According to our measurements, the chemical composition of the PAA films has only a minor influence on the coloring and the increase of the optical density, and that the light absorbing properties mostly likely result from the
Electronic devices have been widely used by modern people for everyday life and industry. To achieve both portability and performance goals, devices have become increasingly smaller and more highly integrated, making them more susceptible to interference from electromagnetic waves. To prevent this, there is an increasing demand for an electromagnetic shielding film which is lightweight, thin, and excellently absorbs electromagnetic wave. In case of the nano-fiber which has one-dimensional structure, the electrical conductivity increases and it can be positively affected to absorb an electromagnetic wave. We have fabricated the composite nanofibers including iron, nickel and zinc nitrate using electrospinning method which can easily make a uniform fiber structure. The composite nanofibers were heat-treated to volatilize and crystallize to obtain Ni3Zn5Fe2O4 spinel ferrite phase, and its microstructure, crystal phase, and magnetic hysteresis loop were analyzed. The spinel ferrite phase and average diameter of ~200 nm in Ni3Zn5Fe2O4 nanoparticles were confirmed by X-ray diffraction and field-emission scanning electron microscope, respectively. The magnetic properties of Ni3Zn5Fe2O4 nanofibers with average diameter were observed through the vibrating sample magnetometer. The film to absorb an electromagnetic wave was fabricated using the Ni3Zn5Fe2O4 nanofibers as a filler. The absorbing properties of 11 dB at 10 GHz were measured by a vector network analyzer. The microstructure of the Ni3Zn5Fe2O4 nanofibers was optimized and suggested to apply to electromagnetic wave shielding.

**EP02.05.06**

Controlling the Surface Chemistry of Quantum Confined Silicon Nanoparticles for NIR to Visible Upconversion Carter S. Gerke and Pan Xia; University of California, Riverside, Riverside, California, United States.

Silicon nanoparticles have large absorption coefficients compared to the bulk while also being highly emissive with reported photoluminescent quantum yields as high as 90%. These nanoparticles would be of great interest as sensitizers for triplet fusion based photon upconversion to convert low energy light from the NIR window into the visible spectrum. Photosensitized triplet excitons can be harvested from the nanoparticle by grafting organic transmitter ligands to the surface of the Si nanoparticle. These bound transmitter ligands will mediate energy transfer from the nanoparticle, and ultimately to a free molecular emitter. The emission wavelengths from this upconversion platform will be highly tunable by altering the layers of conjugation in the organic ligands i.e. perylene to anthracene to tetracene. These silicon nanoparticle systems would be useful for light sensitized biological disciplines as it is biologically benign and the NIR excitation light is physically transparent allowing for high penetration depths.

**EP02.05.07**

New Findings on GaAs:Mg Micro-Pyramidal Structures Base Solar Cells by Morphological Study Leon Hamui; Engineering, Anahuac University, Mexico City, Mexico.

We studied GaAs:Mg doped nanostructures grown by MBE on GaAs (001) oriented substrate. A pyramidal structure (~3–10 Microns) has been obtained for several deposition conditions and varying the temperature it has been observed a change on the density of these pyramids. Complementary to direct optical imaging by microscope, Confocal Raman Spectroscopy which is widely applied to study nanostructures, has been used to determine the different phonon modes presented. In order to study the pyramidal structures, Confocal Raman Spectroscopy analysis of the surface allows profiling the Raman intensity of the different phonon modes over a scan area. Raman spectroscopy allows not only structural parameters such as superlattice periodicity and layer composition to be determined, but also by scanning it provides information of the pyramidal structures size, shape and strain. Moreover, we have been able to scan an area with depth profiles giving as a result a stack used to obtain 3D (tomographic) spatial information of the sample. Therefore we were able to determine the composition and strain of the pyramids via 3D imaging compared to the flat film area. Although, it has been observed by Raman Spectroscopy that the GaAs TO signal is downshifted due to the Mg doping which is more intense with-in the pyramid area, indicating that the micrometric structures are mainly related to the incorporation of Mg to the GaAs. The confocal area image was color pattern for the different phonon modes to be able to study the growth of the pyramidal structure and relate it to the deposition temperature.

SESSION EP02.06: Photonic Materials and Devices for Biointerfaces IV
Session Chairs: Anthony Banks and Xing Sheng
Thursday Morning, April 25, 2019
PCC North, 200 Level, Room 223

8:30 AM *EP02.06.01
Conformal Electrodes for Electrophysiological Monitoring Xiaodong Chen; Nanyang Technological University, Singapore, Singapore.

Microelectrode arrays, which interface living tissues with electrical hardware, constitute powerful tools for the transduction of original electrochemical signals in living tissues to electronic-based currents in external electrical circuits, and vice versa. They play a vital role in promoting the understanding of underlying physiological mechanisms, as well as improving diagnostics and therapy of neurological disorders and disabilities. However, the crucial aspects toward the advancement of this direction include the development of mechanically durable microelectrodes, facile fabrication, diminished foreign-body response, conformable electrodes and circuits, and so on. In this talk, I will present our latest progress in rational design of conformal electrodes for electrophysiological monitoring.

9:00 AM *EP02.06.02
Highly Integrative Optical Components for Lab-in-a Tube and Microrobotic Systems Oliver G. Schmidt; Leibniz IFW Dresden, Dresden, Germany.

On-chip fabricated rolled-up microtubes act as ultra-compact components in fully integrative lab-in-a tube systems for single cell analysis [1]. These microtubes are equipped with photonic functionalities to generate new types of optofluidic and opto-plasmonic components for novel sensing and detection schemes in 3D microtubular optical cavities [2,3]. Microtubes also sit at the core of microrobots, which in the ultimate limit should perform relevant biomedical tasks in the human body. However, tracking and imaging medical microrobots in deep tissue represent a major challenge in this field [4]. A decisive step in tackling this challenge will be presented in the talk.

Patterning Vertically-Grown Gold Nanowire Arrays for Intrinsically Stretchable Electrodes

Bowen Zhu, fiance Lin, Shu Gong and Wenlong Cheng; Monash University, Melbourne, Victoria, Australia.

Advances in large-area organic electronics for electronic skins and biointerfaces demand highly stretchable, patternable and conformal electrodes to minimize contact resistance when sensors such as pressure sensors are mechanically deformed. Gold is an excellent electrode material with work function matching well with p-type organic transistors. However, it is non-trivial to fabricate highly stretchable gold electrodes for stretchable organic electronics. Here by combining the advantages of both top-down patterning and bottom-up synthesis, we introduce a new materials platform of patterned vertically-grown gold nanowires (AuNWs) for constructing intrinsically stretchable electrodes, with high conductivity of 1,288 S/cm at 0% and 152 S/cm at 170% strain. Such patterned vertical AuNWs can be embedded in elastomer matrix, leading to stretchable electrodes that are mechanically robust and durable. The interface between AuNWs electrodes and poly(3-hexylthiophene) (P3HT) thin film shows ohmic contact for the entire strain regime from 0% to 100%, indicating low contact resistance. We further demonstrate a stretchable organic transistor with ion gel as dielectric, which can survive up to 100% without much performance degradation. The results presented here indicate that our methodology may be extended to other organic semiconducting materials and devices, hence, offering a general electrode materials platform for devising high performance intrinsically stretchable organic electronics.

9:45 AM EP02.06.04
Femtosecond Laser Micromachining on Multifunctional Polymer Fiber-Based Neural Probes for Multisite Chronic Neural Interfacing
Shan Jiang1, Yuanyuan Guo2, Jongwoon Kim1, Shuo Yang1, William A. Mills III1, Anbo Wang1, Ian Kimbrough1, Harald Sontheimer1 and Xiaotong Ju1; 1Virginia Tech, Blacksburg, Virginia, United States; 2Tohoku University, Sendai, Japan.

In order to understand the functional network in the brain and to treat brain-related disorders effectively, it is of great importance to discover the relationship between different brain regions, and many technologies have been developed based on that need. The widely adopted neural interfacing devices are metal-based microwires and silicon-based multichannel arrays, which have excellent recording capability with high signal to noise ratio. However, the mechanical property mismatch between these rigid devices and soft brain tissue can lead to neuron death and device failure in long term implant. Recently, polymer fiber-based neural probes have shown advantages over conventional neural interfaces in terms of flexibility and biocompatibility. However, so far the functions of fiber-based probes have been restricted to the tip area, significantly limiting the application of these devices. Here we present the femto-second laser micromachining on the longitudinal surface of the multifunctional polymer fiber, which can expose multisite electrodes, microfluidic channels, and waveguides along the fiber length. Using this micromachining technique, we can pattern the fiber surface with arbitrary geometry and spacing on the fiber longitudinal surface with a submicron resolution. Therefore, we can investigate different brain regions’ responses toward stimulation at different locations, and have a better understanding of the signal correlation in between. In this study, we performed simultaneous optical stimulation and multisite electrical recording in transgenic mouse brain using a single fiber probe, and analyzed the correlation between the signals recorded from different brain regions. We also patterned microfluidic channels and delivered fluorescence dyes into multiple locations in the brain, which can be used for multisite drug delivery in the brain. Furthermore, chronic recording and long term tissue responses were examined to evaluate our multifunctional neural probes as chronic neural interface devices. The femtosecond laser micromachining significantly expands the capability of multifunctional fiber-based neural interfaces, which can lead to wide applications in neuroscience.

10:00 AM BREAK

10:30 AM *EP02.06.05
New Forms of Microscopy Enabled by Nanostructured Surfaces
Brian Cunningham; Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Since the advent of optical microscopy, a flat glass microscope slide has been the standard surface upon which tissues, cells, and biomolecules are attached for observation. Recently, we have utilized the optically resonant properties of nanostructured photonic crystal (PC) surfaces to enable several new microscopy modalities where the nanostructure provides new forms of contrast for a wide variety of compelling applications. By designing PC surfaces with resonances that match the excitation and emission spectra of photon emitters such as fluorophores and quantum dots, PC enhanced fluorescence (PCEF) microscopy reduces the detection limits of any surface-based fluorescence assay. By generating spatial images of the PC resonant reflection intensity, we can selectively and dynamically visualize the cell-extracellular matrix interface during processes that include stem cell differentiation, cancer cell response to drugs, and chemotaxis – including the ability to observe the formation and evolution of cell membrane focal adhesion sites. We call this approach Photonic Resonator Outcoupler Microscopy (PROM), as we observe highly localized outcoupling of light from the PC that occurs due to scattering by dense regions in the cell membrane. Further, by utilizing metallic nanoparticle tags with plasmon resonances that match the PC resonance, we obtain highly efficient coupling of light into nanometer-scale electromagnetic hotspots, that is accomplished by highly localized “quenching” of the PC reflection efficiency, which we use for digital-resolution detection of miRNA biomarkers for cancer with 100 aM limits of detection, using an approach called Photonic Resonator Absorption Microscopy (PRAM). The seminar will describe the physical principles, nanostructure design/fabrication, instrumentation, and applications for nanostructure-enabled microscopy for disease diagnostics, personalized medicine, and life science research.

11:00 AM *EP02.06.06
Graphene-Related Materials for Electronic Skins
Guozhen Shen; Institute of Semiconductors, CAS, Wuhan, China.

Electronic skin (e-skin) which can mimic pressure, humidity, and temperature sensing capabilities of human skin has obtained great attention due to its superior abilities to detect slight pressure changes. It has potential application in human health monitoring, medical diagnostics, tactile sensor, artificial intelligence, and so on. Graphene, as a novel 2D carbon nanomaterial, possesses excellent characteristics which are required for E-skins, such as the good electrical property, high thermal conductivity, chemical stability, and good mechanical strength. In this talk, I will briefly introduce our recent progress on fabricating high performance e-skins with graphene-related materials. By wrapping reduced graphene oxide (rGO) nanosheets on PVDF nanofibers, a planar piezoresistive tactile sensor was fabricated, exhibiting a high sensitivity of 3.1 kPa−1 in very low pressure regime (below 60 Pa) and 15.6 kPa−1 in high-pressure regime (above 20 kPa). Using the same material, we further fabricated a multifunctional e-skins. Four kinds of planar devices namely micro-supercapacitors, pressure sensor, photodetector and gas sensor were modularly manufactured, all with rGO encapsulated PVDF nanofibers as the functional materials. Inspired by these works, we also fabricated other kinds of high performance e-skins.

11:30 AM EP02.06.07
Textured Si Nanowires for Highly Localized Optical Modulation of Cellular Dynamics
Yin Fang1, 2, Yuanwen Jiang1, 2 and Bozhi Tian1, 2; 1JFI, University of Chicago, Chicago, Illinois, United States; 2Department of Chemistry, University of Chicago, Chicago, Illinois, United States.

Engineered silicon-based materials display photoelectric and photothermal responses when illuminated by light, which allows for innovation at silicon-biology interfaces. Silicon nanowires have small radial dimensions, which are promising for use as highly localized cellular modulators. However, so far the functions of silicon nanowire materials have been restricted to the tip area, significantly limiting the application of these devices. Here we present the femtosecond laser micromachining on the longitudinal surface of the multifunctional polymer fiber, which can expose multisite electrodes, microfluidic channels, and waveguides along the fiber length. Using this micromachining technique, we can pattern the fiber surface with arbitrary geometry and spacing on the fiber longitudinal surface with a submicron resolution. Therefore, we can investigate different brain regions’ responses toward stimulation at different locations, and have a better understanding of the signal correlation in between. In this study, we performed simultaneous optical stimulation and multisite electrical recording in transgenic mouse brain using a single fiber probe, and analyzed the correlation between the signals recorded from different brain regions. We also patterned microfluidic channels and delivered fluorescence dyes into multiple locations in the brain, which can be used for multisite drug delivery in the brain. Furthermore, chronic recording and long term tissue responses were examined to evaluate our multifunctional neural probes as chronic neural interface devices. The femtosecond laser micromachining significantly expands the capability of multifunctional fiber-based neural interfaces, which can lead to wide applications in neuroscience.

References:
Enabling Intracellular Recordings on Commercial High-Density Multi-Electrode Arrays by Optoacoustic Poration and Meta-Electrodes

Michele Dipalo1, Giovanni Melle1, Laura Lovato1, Andrea Jacassi1, Valeria Caprettini1, Francesca Santoro1, Denis Garoli1, Francesco Tantussi1, Giulia Bruno1, Alessandro Alabastri1 and Francesco De Angelis1
1 Istituto Italiano di Tecnologia, Genova, Italy; 2 Rice University, Houston, Texas, United States.

The accurate monitoring of cell electrical activity is of fundamental importance for pharmaceutical research and pre-clinical trials that impose to check the cardiotoxicity of all new drugs. Such a strong interest stimulated the development of methods for intracellular recording of action potentials on a large scale. Currently, the most promising results are represented by multi-electrode arrays (MEA) refined with 3D nanostructures that were introduced in pioneering seminal papers1,2, culminating with the recent work from the group of H. Park2, who show intracellular recordings on high-density CMOS-based MEA refined with 3D nanopillars. However, the requirement of 3D nanostructures limits the practical exploitation of these techniques. First, the fabrication of 3D nanopillars is an extremely complex and expensive procedure, hardly applicable to large area production. Second, cells’ interaction with 3D nanopillars is still under investigation3-6, with unresolved questions about their interaction, especially in case of mechanically contracting cardiomyocytes. Finally, most of the works exploited electroporation, which complicates considerably the circuit design of high-density CMOS circuits. Thus, despite pioneering results have been obtained on both passive and active MEAs, these technologies have not yet been applied to practical cases nor reached the commercial phase. Here, we introduce the concept of planar meta-electrodes and we show for the first time that high quality intracellular signals can be recorded on high-density commercial CMOS-MEAs without any rework of the devices, with 3D nanostructures nor circuitry for electroporation7. The intracellular recording is obtained by means of laser optoacoustic poration mediated by a meta-electrode, which is a porous platinum electrode with a dual optical/electrical function. Optically, it behaves like a strong broadband absorber in the near-infrared, as it has been recently shown for metasurfaces in general8. Electrically, it provides strong cell coupling due to the tight sealing of the cell membrane on the porous morphology. When illuminated with a short laser pulse, the plasmonic response of porous platinum enables the generation of localized high electric field hot-spots that produce shockwaves9-10 able to open the cell membrane. This enables high quality intracellular recordings with no side effects. We will show sharp intracellular action potentials of human derived cardiomyocytes on a commercial CMOS-MEA. To prove the direct application to pharmacological screening, we will also show the exploitation of our approach to detect the effects of typical drugs and toxins on the cell cultures, thus confirming the high potential of the technique to improve pharmaceutical tests. The technique offers lower development and recurring costs due to the “already commercial” nature of the employed devices. Our work paves the way to a completely new set of affordable and effective methods for studying electrogenic cells. Moreover, the new meta-electrodes may have extreme impact on combining optical and electrical investigations for biochemistry and biology that require today new multifunctional tools11.

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Engineering Transparent Graphene Microelectrodes to Overcome Quantum Capacitance Limit

Yichen Lu, Xin Liu, Ryonna Hattori, Chi Ren, Xingwang Zhang, Takaki Komiyama and Duygu Kuzum; University of California, San Diego, La Jolla, California, United States.

Substantial progress has been made in development of graphene-based transparent optical interfaces enabling concurrent integration of electrophysiological recordings, optical imaging and optogenetics. However, a big challenge toward the transparent graphene electrodes is relative high, limiting its scalability and its use for microstimulation. As a result, high impedance of graphene constitutes a big challenge toward the widespread use of transparent electrodes. Here, we experimentally investigate the origins of high impedance in graphene microelectrodes and demonstrate that the impedance of graphene microelectrodes is fundamentally limited by quantum capacitance. We overcome this quantum capacitance limit by creating a parallel conduction path using electrochemically deposited platinum nanoparticles. This approach achieves a 100 times reduction in graphene electrode impedance, while maintaining the high optical transparency crucial for deep two-photon microscopy. Using a transgenic mouse model, we demonstrate simultaneous electrical recording of cortical activity with high fidelity while imaging calcium signals at various cortical depths right beneath the transparent microelectrodes. Multimodal analysis of Ca2+ spikes and cortical surface potentials offers unique opportunities to bridge our understanding of cellular dynamics and brain-scale neural activity.

Plasmonic Response of Light-Activated, Nano-Gold Doped Polymers

Jessica M. Andriolo1,2, McKenzie L. Joseph1,2, Mark Griep3 and Jack L. Skinner1,2; Mechanical Engineering, Montana Technological University, Butte, Montana, United States; 1,2 Montana Nanotechnology Laboratory, Montana Technological University, Butte, Montana, United States; 3, U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Incorporation of metallic nanoparticles (NPs) in polymer matrix is well known to be employed to enhance and control dissolution and release of drugs, for targeted drug delivery, antimicrobial agents, localized heat sources, mechano-responsive nanocomposites, and for unique optoelectronic applications. Colloidal gold NPs (AuNps) in particular exhibit a plasmonic response that can be utilized for photothermal applications. Dispersion of Au nanoparticles in polymers creates a hybrid material with increased robustness, responsiveness, and flexibility while intrinsic nanoparticle properties are maintained. In previous work, colloidal gold (AuNps) were incorporated into electrospun (ES) polyethylene glycol fibers (AuNps/PEG) to utilize the nanoparticle plasmonic response for localized heating of the polymer. Applications of this work were anticipated for localized heating and melting of drug-carrying polymer fibers for light-activated release. Using broad spectrum white light interrogation, the AuNps used exhibited a maximum absorbance at 522 nm on ultra violet visible spectroscopy (UV-Vis) which was the same when AuNps was incorporated into bulk polymer (AuNps/PEG8000 MW). Using trapezoidal integration of the energy absorption difference curve, the theoretical energy absorption for AuNps/PEG was calculated to have an efficiency enhancement of 9.6% under white light illumination and 38.3% under green light illumination compared to PEG alone. Maximum absorbance of these materials in fiber form was recorded at 504 nm. AuNps/PEG fibers were ES directly onto resistance temperature detectors (RTDs) so that resistance of the materials could be measured. To maximize the response of the polymer, white light was substituted for green laser light (λ=533 nm), and resistance measured was converted to optical, thermal-cycling and delamination effects. The encapsulation acts as a thermal insulator, so if it is too thin, there can be hot-spots at neighbouring electrodes. However, bond wires and bonded surface components such as the photonic microemitters need encapsulation to prevent shorting between anode and cathode contacts by the saline. As such, we encapsulate our system in poly-dimethyl-siloxane. For acute research purposes, electronics fabricated from standard complementary metal oxide semiconductor (CMOS) processes, can rely on the silicon oxy-nitride top layer. We have demonstrated efficacy of our optoelectronic probes in the acute setting and with recordings and stimulus on both rodent and non-human primate animal models. We are placing active electronics which can multiplex hundreds/thousands of optical and/or electrical interfaces.

Developing Clinical Grade Implantable Optoelectronics

Patrick Degenaar; Newcastle University, Newcastle upon Tyne, United Kingdom.

Implantable electronic systems are being increasingly utilised to provide therapeutic benefit. Exemplars include pacemakers for the heart and brain, neuromodulators for bladder and pain control, and sensory prosthetics for sound and vision. Traditionally such systems would comprise two primary units: A hermetic case which contains the control electronics, and a lead with electrodes which provide recording or stimulus. Such systems are typically limited to a few dozen electrodes, as such, there is now a strong interest in placing active electronics which can multiplex hundreds/thousands of optical and/or electrical interfaces.

In Newcastle University, we are developing a new type of clinical-grade implantable device to prevent seizures in patients with focal, drug-resistant epilepsy, and a project called CANDO. We are utilising a gene therapy technique called optogenetics which renders the brain tissue light sensitive. We can then electrically record and optical stimulate at the brain unit. However, we have chosen our brain unit to consist of active electronics, to allow for multiplexing of multiple optical stimulation points whilst simultaneously recording. The CANDO control unit is similar to others in the domain – i.e. battery and control electronics sitting in a hermetic case with hermetic feedthroughs to cables connecting to a brain unit. However, we have chosen our brain unit to consist of active electronics, to allow for multiplexing of multiple optical stimulation points whilst simultaneously recording. The active electronics is fabricated from a standard complementary metal oxide semiconductor (CMOS) process by a foundry (Austria Microsystems) under a commercial process. The chips have been designed to incorporate a digital communication and control scheme as well as drive electronics for individual light emitting diodes, self-diagnostic circuitry, and amplifiers and analog to digital converters to acquire neural signals. The active electronics connect to penetrating shafts with electrodes and optical microemitters to stimulate.

Developing Clinical Grade Implantable Optoelectronics

We have demonstrated efficacy of our optoelectronic probes in the acute setting and with recordings and stimulus on both rodent and non-human primate animal models. We are now beginning long term chronic animal studies to understand the efficacy of different control algorithms for preventing seizures. For acute research purposes, electronics fabricated from standard complementary metal oxide semiconductor (CMOS) processes, can relax the silicon oxy-nitride top layer. However, bond wires and bonded surface components such as the photonic microemitters need encapsulation to prevent shorting between anode and cathode contacts by the saline. As such, we encapsulate our system in poly-dimethyl-siloxane.

There are important considerations in the design of encapsulation of such devices:

Insulation and hot spots: Light emitting diodes are typically 5-40% efficient. The rest of the energy provided to them is emitted as heat. However, the regulations state that the surface of implantable devices should not exceed 2°C. The encapsulation acts as a thermal insulator, so if it is too thin, there can be local hot-spots above the LED. However, if it is too thick, there can be hotspots at neighbouring electrodes.

Failure mechanisms: Implantable devices need to last perhaps decades to last a human lifetime, perhaps decades in the brain. We are therefore exploring accelerated lifetime studies of failure modes including optical, thermal-cycling and delamination effects.
Nanostructure-Enhanced Devices for Flexible and High-Performance Electronics and Optoelectronics - Zhiyong Fan; Department of Electronic and Computer Engineering, Hong Kong University of Science and Technology, Hong Kong, China.

Nanostructured materials possess a number of unique properties such as tunable optical and electronic property, high surface-to-volume ratio, mechanical flexibility, etc. These intriguing properties can be harnessed for a variety of applications in flexible electronic and photonic devices. In the past, we have fabricated an assortment of nanostructures that consist of nanowires, nanopillars, nanocubes, etc., using a variety of materials from inorganic semiconductors to organic-inorganic hybrid materials. These nanomaterials/nanostructures have been fabricated into a variety of functional devices including solar cells, supercapacitors, light-emitting diodes, gas sensors, etc. By manipulating light and charge interactions with nanostructures, the performance of these devices can be largely tuned. And if the nanostructures are rationally designed, the performance of devices can be significantly improved. Here we will present the fabrication methods of nanostructures and design rules of nanostructures for these high performance electronic and optoelectronic device. And the integration of these devices into concept proof wearable systems will also be demonstrated.
Biodegradable and Biocompatible Microelectromechanical Systems

Mark G. Allen; Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Fabrication approaches to biodegradable and biocompatible microelectromechanical (MEMS) devices suitable for implantation in the body will be discussed. Three topical areas will be touched upon: biodegradable wireless pressure sensors; biodegradable batteries; and MEMS fabricated from protein materials.

Biodegradable Wireless Pressure Sensors: A wireless pressure sensor made entirely of biodegradable materials will be discussed. Such biodegradable sensors may be appropriate for short-term, acute medical implantation applications as they potentially eliminate the need for implant extraction when sensing is no longer required. Metallic bilayers with controllable corrosion characteristics are utilized as conductors, and biodegradable polymers poly-L-lactide (PLLA) and polycaprolactone are used as dielectric and structural materials. The fabricated sensor is based on a resonant variable capacitance technique and was wirelessly tested in both air and 0.9% saline. The sensor exhibited a linear resonant frequency response to external applied pressure, over the physiologically-relevant 0-20 kPa applied pressure range. Sensors remained stable and functional for approximately 86 hours in saline solution.

Biodegradable Batteries: Implantable and biodegradable batteries play an important role in the fully degradable medical systems; however, in such systems compactness and energy density are of great importance. Harnessing liquid from the body to serve as the battery electrolyte may, therefore, be desirable; however, for stable operation, maintaining a constant environment inside the electrochemical cell is required even in the presence of changing body conditions. A biodegradable battery featuring a solid electrolyte of sodium chloride and polycaprolactone will be discussed. This approach harnesses the body fluid that diffuses into the cell as an element of the electrolyte; however, the large excess of sodium chloride suspended in the polycaprolactone holds ionic conditions inside the battery relatively constant. A constant discharge profile can then be achieved even in the presence of varying external aqueous conditions, enabling compact, stable-performing cells.

Protein MEMS: The use of extracellular matrix (ECM) protein materials in the fabrication of MEMS offer the possibility of MEMS-based devices that are more easily integrated with the body, are better tolerated by the immune system, and/or which have mechanical properties that are well-matched to potential biological applications. However, the incorporation of these relatively delicate materials into standard MEMS fabrication processes can result in significant fabrication challenges. Suitable fabrication approaches to Protein MEMS will be discussed, and their use will be illustrated in a collagen-based cortical neural electrode, which has demonstrated reduced inflammation and superior persistence of functionality in in vivo models when compared to similarly-sized MEMS electrodes fabricated from conventional materials.

Fully Biodegradable Batteries for Self-Powered Transient Implants

Lan Yin and Xueying Huang; Tsinghua University, Beijing, China.

Biodegradable transient devices is an emerging type of electronics that could play an essential role in medical therapeutic/diagnostic processes, such as wound healing, tissue regeneration, etc. The associated biodegradable power sources, however, remain a major challenge towards future clinical applications, as the demonstrated electrical stimulation and sensing functions are limited by wired external power or wireless energy harvesters via near-field coupling. We propose novel materials strategies and fabrication schemes that enable a high-performance fully biodegradable magnesium-molybdenum trioxide battery as an alternative approach for in vivo on-board power supply. The battery can deliver a stable high output voltage as well as prolonged lifetime that could satisfy requirements of representative implantable electronics. The battery is fully biodegradable, and demonstrates desirable biocompatibility. The battery system provides a promising solution to advanced energy harvesters for self-powered transient bioresorbable implants as well as eco-friendly electronics.

Bioresorbable Electronics for Minimally Invasive Medical Sensing and Treatment of Nervous System

Seung-Kyun Kang; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Nanoscale thin-film technology has opened an era of soft, flexible and stretchable electronics and has also changed the timescale of dissolution of materials. Silicon nanomembranes of 10-100 nm thickness have dissolution behavior on the order of days to months. This feature lets us construct Si electronics for water-soluble and biodegradable performance using unusual fabrication processes and combining soft/biodegradable polymers. Here we introduce two representative examples of bioresorbable Si electronic devices useful in monitoring and modulating the nervous system. First, a bioresorbable pressure sensor using piezoresistive Si strain gauge and 3D microstructured diaphragm was demonstrated to provide accurate measurement of intracranial pressure during the incubation period of traumatic injury. Wireless interfaces made of polymer-coated bioresorbable metal strips offer stable and continuous pressure monitoring. In-vivo functional and immunotoxicological demonstrations in a rat model suggests the potential validation of bioresorbable sensors in the clinical stage. In the other example, bioresorbable wireless electrical stimulator interfacing the peripheral nerve was demonstrated as a therapeutic modulator. An integrated circuit of Si diode, capacitor, and inductor with all-biodegradable metal, semiconductor and dielectric materials generate therapeutic electrical pulses by near-field inductive energy transfer. The accelerated functional recovery of transected nerve with electrical stimulation suggests the capability of bioresorbable stimulator to promote and/or modulate the nervous system in the treatment and rehabilitation stage.

Digitally Inkjet-Printed Electro(Fluoro)Chromic Devices Consisting of Biodegradable and Biocompatible Materials

Manuel Pietzsch1,2, Martin Held1,2, Luca Porcarelli3, Ana Sanchez-Sanchez4,5, David Mecerreyes1 and Gerardo Hernandez-Sosa1,2 – 1, LIT, Karlsruhe Institute of Technology, Karlsruhe, Germany; 2InnovationLab, Heidelberg, Germany; 3POLYMAT, University of the Basque Country UPV/EHU, San Sebastian, Spain; 4Bioelectronics Laboratory, University of Cambridge, Cambridge, United Kingdom.

Electrofluorochromic devices (EFCD) receive increasing attention in investigation in the past years, because they offer the possibilities for various optical devices. Besides that, the little power consumption, the low voltage requirement and simple device architecture (i.e. electrochemical cell) provide the opportunity for low-cost display devices. To provide a cost-effective method with the freedom of design necessary for smart windows and display applications, inkjet printing can be used as a suitable method with high throughput, low-material waste and up-scaling capabilities to industrial fabrication. These exceptional properties can be extended with the use of bioresorbable and biodegradable materials for their use in medical applications or to reduce the waste after usage to a minimum.

Here, we report on inkjet-printed electro(fluo)chrome devices consisting of biodegradable and biocompatible components on biodegradable deformable gelatin substrates. To simplify the device architecture for the inkjet printing process we chose a parallel electrode configuration with PEDOT:PSS as electrode material. We used two different solid polymer electrolytes, one on the basis of gelatin coated from water and the other on the basis of Poly(D,L-lactide-co-glycolide) (PLGA) from a Dimethyl sulfoxide (DMSO) solution, whereby all of these polymers and solvents are biodegradable and biofriendly. As ionic species we used tetrabutylammonium bis-oxalato borate (TBABOB) which was developed as a non-fluorinated biodegradable salt. The electro(fluo)chrome layers were made out of two different polymer derivatives consisting triarylamine, namely polyyindeno-fluorene-8-triarylamine (PIF8-TAA) and polytriarylamine (PTAA). The fabricated devices exhibit a sufficient contrast, efficiency and lifetime to be used in deploy-and-forget or short-life-lifecycle applications with potential use in disposable consumer and health care biofriendly disposable applications.
Skin-Inspired Organic Electronics Zhenan Bao; Stanford University, Stanford, California, United States.

Flexible organic electronics have attracted considerable attention over the past decade. Stretchable electronics represent another type of optoelectronic devices that are intrinsically elastic, that is they are foldable, twistable, and stretchable while maintaining performance, integrity and durability. Incorporated into devices, properly designed stretchable materials may result in more robust devices under bending and strain compared to flexible but not stretchable materials. For intrinsically stretchable electronics, it is desirable to have intrinsically stretchable materials, ranging from stretchable conductors, stretchable dielectric to stretchable semiconductors. In this talk, I will present various molecular design concepts for realizing stretchable electronic polymers without compromising electronic properties. Their applications in bioelectronics will also be presented.

Flexible Bioelectronics—Enzyme-Based Body-Worn Electronic Devices Joseph Wang; University of California, San Diego, La Jolla, California, United States.

Wearable bioelectronic devices rely on oxidoreductase enzymes and have already demonstrated considerable promise for on-body applications ranging from highly selective non-invasive biomarker monitoring to epidermal energy harvesting. Critical to such success is the judicious design of the enzyme-electronic interface, along with flexible platforms with mechanic properties similar to those of biological tissues. Such devices require special attention to the enzyme-electronic interface and to several considerations related to wearable applications, such as mechanical properties (flexibility and stretchability), operational stability in different biofluids and under changing conditions (e.g., pH, temperature), biofouling, selectivity, and biofouling. Keeping these requirement in mind, our group has pioneered a variety of wearable biocatalytic sensors and biofuel cells devices. By leveraging the advantages of biocatalysis, electrochemistry, and flexible electronics, and addressing key challenges, wearable bioelectronic devices could have a tremendous impact on diverse biomedical, fitness and defense fields.

References


Recently emerging classes of battery free, ultrasmall1, fully implantable devices for optogenetic neuromodulation2 eliminate physical tethers associated with bulky head-stages and batteries in alternative wireless technologies and conventional setups by leveraging cellular scale light emitting diodes on flexible injectable filaments as light sources1. These highly miniaturized systems enable untethered, operation for behavioral studies that eliminate motion constraints and enable new experimental paradigms in a range of complex 3D environments and contexts (e.g. social interactions) that cannot be explored with conventional technologies. These devices are, however, purely passive in their design, thereby precluding any form of active control or programmability, resulting in limitations when investigating circuit dynamics where independent operation of multiple light sources with precise active control is needed. Here we present a series of important concepts that enabled controlled device operation, independent of position and angle relative to the experimental arena, with advanced wireless power harvesting capabilities and full user-programmability over multiple devices. This level of functionality is demonstrated in integrated platforms that are compatible with noninvasive imaging technologies such as computed tomography and magnetic resonance imaging and have sizes and weights not significantly larger than those of previous, passive systems. The resulting devices qualitatively expand options in brain tissue illumination for optogenetic neuromodulation and multimodal operation, with broad potential applications in neuroscience research, with specific advances in precise dissection of neural circuit function during unconstrained behavioral studies.

References

On-skin sensors have attractive much attention as the next-generation wearable devices, because the conformal contact on human skin enables accurate and continuous detection of physiological signals. One of the most important technologies to improve usability of on-skin sensors is a power source to continuously supply electricity to health-monitoring systems. In this talk, we will report on recent progresses of ultraflexible organic photovoltaic cells for applications to wearable sensors. First, ultraflexible organic power sources that can be wrapped around an object have been developed with mechanical and thermal stability in long-term operation. Then, the integration of these power sources with functional electric devices including sensors has been achieved.

Recent studies have demonstrated that in addition to biochemical and genetic interactions, cellular systems also respond to biophysical cues, such as electrical, thermal, and mechanical signals. However, we only have limited tools that can introduce localized physical stimuli and/or sense cellular responses with high spatiotemporal resolution. Inorganic semiconductors display a spectrum of physical properties and offer the possibility of numerous device applications. My group integrates material science with biophysics to study several semiconductors-based biointerfaces. In this talk, I will first pinpoint domains where semiconductor properties can be leveraged for biointerface studies, providing a sample of numbers in semiconductor-based biointerfaces. Next, I will present a few recent studies from our lab and highlight key biophysical mechanisms underlying the non-genetic optical modulation interfaces. In particular, I will present a biology-guided two-step design principle for establishing tight intra-, inter-, and extracellular silicon-based interfaces in which silicon and the biological targets have matched mechanical properties and efficient signal transduction. Finally, I will discuss new materials and biological targets that could catalyze future advances.

Organic electronic devices, apart from consumer applications, are presently paving the path for key applications at the interface between electronics and biology. In such applications, organic polymers are very attractive candidates, due to their distinct properties of mechanical flexibility, self-healing and mixed conduction. My group investigated the processing conditions leading to high electrical conductivity, long-term stability in aqueous media as well as robust mechanical properties of the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrilene sulfonate (PEDOT:PSS) [1-3]. We have demonstrated that stretchable PEDOT:PSS films can be achieved by adding a fluorosurfactant to the film processing mixture and by pre-stretching the substrate during film deposition. We have achieved patterning of organic materials on a wide range of substrates, using orthogonal lithography and pattern transfer [4-5]. Recently we have discovered that PEDOT:PSS films can be rapidly healed with water drops after being damaged with a sharp blade [6] or show autonomous self-healing if processed in presence of certain additives. My talk will deal with processing, characterization and patterning of conducting polymer films and devices for flexible, stretchable and healable electronics. I will particularly focus on the strategies to achieve films with optimized electrical conductivity and mechanical properties, on unconventional micro patterning on flexible and stretchable substrates, on the different routes to achieve films stretchability and self-healing.

Dopamine (DA), as a crucial neurotransmitter, can transfer chemicals in human brain to affect our emotion and behaviors, and DA disorders in secretion and transportation can cause some incurable disease, such as Parkinsonism and Alzheimer’s disease. Implantable flexible sensors offer a feasible approach to monitor the content and distribution of DA, cause some incurable disease, such as Parkinsonism and alzheimer’s disease. Implantable flexible sensors offer a feasible approach to monitor the content and distribution of DA, and may assist us to overcome those disease. Up to now, mainly reported investigations were conducted using electrochemical sensors modified by metallic oxide and graphene, but rough structures and limited types of above materials restrict its further development in function modulation. One of the promising strategy to meet this challenge is employing adjustable materials to combine with flexible sensors, and metal-organic frameworks (MOFs) that possess designable structures and adjustable functions can be considered as the suitable candidate for fabricating functional devices. Additionally, flexible sensors integrated with MOFs have already been achieved by our group, allowing more explorations on MOF-based flexible electronics.

Given the above consideration, this paper presents techniques and materials to fabricate a luminescent MOF-based flexible sensor, and photoelectric detector in the sensor can detect emission changes of MOF represented as functional part in response to DA. Notably, MOF-modified sensor possesses excellent biologically safety that was confirmed using live cell experiments, supplying the foundation for the practical application in living animals. This work represents the first effort in combing luminescent MOFs with flexible electronics.

### SESSION EP03.03: Poster Session: Materials Strategies and Device Fabrication for Biofriendly Electronics

**Session Chairs:** Hui Fang and Lan Yin  
**Tuesday Afternoon, April 23, 2019**  
5:00 PM - 7:00 PM  
PCC North, 300 Level, Exhibit Hall C-E

**EP03.03.01**  
**Application of Active Transiency Mechanism in Design of Biodegradable and Environmentally Friendly Polymeric Electronics**  
Rehanbeh Jamshidi; Mechanical Engineering, University of Hartford, West Hartford, Connecticut, United States  
Reza Montazami; Mechanical Engineering, University of Hartford, West Hartford, Connecticut, United States  
Bozhi Tian; The University of Chicago, Chicago, Illinois, United States  
Fabio Cicoira; Chemical Engineering, Polytechnique Montréal, Montréal, Quebec, Canada  
Gus Hall; Chemical Engineering, University of Tokyo, Tokyo, Japan  
Kazuhiro Kojima; RIKEN Center for Emergent Matter Science, Saitama, Japan

Transient materials/electronics is an emerging class of functional devices that are capable of undergoing rapid degradation at prescribed time and controlled rate once transiency is triggered. Application of these materials in circuit boards and environmental sensors eliminates the need for their retrieval, thus minimizing electronic waste production. Transiency rate in solvent-triggered devices is strongly dependent on the chemical composition of the constituents, as well as their interactions with the solvent, upon exposure. Such chemical interactions are typically slow, passive, and diffusion-driven. In this study, we present integration of gas forming reactions into transient materials/electronics to achieve selective, expedited, controlled, and active transiency. Integration of more complex chemical reaction paths to transiency, not only increases selectivity of the process, but also enhances pre-transiency chemical stability of the system while under operation. A proof-of-concept transient electronic device, utilizing sodium-bicarbonate/citric-acid pair as gas forming agents is studied vs. control devices, consisting of polymeric substrate and metal colloid as electronic component, in the absence of gas forming agents. While exhibiting enhanced transiency behavior, substrates with gas forming agents also proved sufficient to be applied as substrates, concerning pre-transiency mechanical properties and...
Biopolyimides for Transparent Insulators

Shrini S. Chhatre, Vivek Subramanian, Nicholas Valdes, Bruce Chase and David C. Martin; Material Science and Engineering, University of Delaware, Newark, Delaware, United States.

Polyimides have been widely investigated for use in a variety of applications including photovoltaics, sensors and electrochromic displays. However, they have been of particular interest to the biomedical community because of their simultaneous electronic and ionic conductivity. They also are mechanically softer than inorganic materials, making it possible for them to be more compatible with living wet tissues. Poly(3,4-ethylenedioxythiophene) (PEDOT) and its copolymers, including the polymer formed from the carboxyl-substituted monomer P(EDOTacid), have been of specific attention because of their chemical stability and excellent charge transport properties. Despite the continued interest in PEDOT, there are still many unknown questions about the details of its polymerization process. One of the major challenges is that PEDOT polymers are relatively insoluble, making an accurate analysis of the degree of polymerization during the reaction difficult.

We have been investigating the use of vibrational spectroscopy techniques along with Gaussian molecular simulations to get a better understanding of the electropolimerization process. The experiments have used microfocused Raman and Fourier Transform Infrared (FTIR) techniques, and compliment ongoing research in our laboratory using in-situ Transmission Electron Microscopy (TEM) and hot stage optical microscopy (OM).

We have identified critical peaks associated with the reactive hydrogens on the thiophene ring that allow us to monitor the process of polymerization. We studied the vibrational modes associated with the reactive proton and conjugation of the thiophene network. The 3110 cm\(^{-1}\) thiophene C=H stretch peaks is of particular interest to us, since it decreases with intensity as the molecules react. In addition, we are monitoring the peak at 1422 cm\(^{-1}\) associated with the C=C stretch and the peaks at 835-1184 cm\(^{-1}\) associated with the conjugation in PEDOT. The peaks at 1540 cm\(^{-1}\) and 1573 cm\(^{-1}\) are associated with the quinoidal structure of the PEDOT. These checks provide insight about the changes occurring during the polymerization reaction. By correlating these vibrational spectroscopic results with data using microscopy, we are developing a deeper understanding of the thiophene electropolymerization reaction.

Honey as Gate Dielectric for Organic Thin-Film Transistor

Oliver Peter Ammuayh1, Kuan Yew Cheong2 and Feng Zhao3; 1Washington State University, Vancouver, Washington, United States; 2Universiti Sains Malaysia, Pulau Pinang, Malaysia.

In this work, natural organic honey as gate dielectric in organic thin-film transistor has been systematically investigated. In recent years, organic materials for electronic applications have gained wide research interests due to their advantages such as environmentally friendly, biodegradable, biocompatible, and do not require chemical synthesis. Thin-film transistor using organic materials as semiconductors (C60, pentacene, etc.), dielectrics (Aloe vera, chicken albumen, benzocyclobutene), and substrates (Silk, PLGA, etc.) have been developed and investigated. This work reports the usage of honey as a gate dielectric layer in a C60-based thin-film transistor. Different curing temperature and duration for honey solidification were applied. Honey film thicknesses under different spin rates and water ratio were measured and compared. MOS capacitors and transistors were fabricated with standard microfabrication processes including photolithography and metal deposition. Effects of solidification conditions of honey including drying temperature and duration on the quality of the honey film such as electrical breakdown, leakage current, hydrophobicity, smoothness, etc. were examined. The results with optimized process parameters and device properties will be reported in the paper and presentation.

Plasma Cleaning of Organics on Bio-mineralized Nanopores

Nishant Satapathy, Srisuda Rojsatien and Michael Goryll; School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States.

The effectiveness of using oxygen plasma to clean the organic residue from bio-mineralized nanoporous valves of marine diatoms (Coscinodiscus wailesii) was investigated. Two plasma processes were employed, one using a commercial 13.6 MHz oxygen plasma cleaner with a maximum plasma power of 30 Watts, the other using a microwave oven with a 2.4 GHz microwave output power of 900 Watts. A reference experiment using photoresist-coated silicon wafers was conducted to determine the etch rate for a planar organic film. While the planar organic layers were being etched in either plasma process, optical microscopy on the actual diatom nanopore frustules showed organic residue (chloroplasts) remaining even for the longest plasma treatment times. This reduced etch rate can be attributed to the shape of the frustules themselves, with the nanopore membrane encapsulating the chloroplast, limiting the diffusion of the reacting species through the nanopores.

Biopolymides for Transparent Insulators

Tatsuo Kaneko and Maiko Okajima; Japan Advanced Institute of Science and Technology, Nomi, Japan.

Bioplastics are indispensable for establishment of green-sustainable society. Conventional bioplastics were composed of aliphatic polymers like poly(lactic acid) having not very high softening temperature and no specific functions. In order to open the world of high-performance bioplastics, we have prepared aromatic biopolymers derived from exotic amino acid. Here we used 4-aminocinnamic acid (4ACA) which was bioavailable by a microorganismal genetic-engineering. The photodimer of 4ACA was successively prepared as a bio-derived aromatic diamine via [2+2] cycloaddition in the solid state with a perfect conversion degree. The biodiamines were polymerized with tetraciod dianhydrides to produce aromatic polyimides. Especially the aromatic polyimides derived from the biodiamine with cyclotpreneetetracarbonlyc dianhydrides, which is also a photodimer of bio-available fumaric acid, showed a good thermomechanical performance as well as low density around 1.05-1.28 g/cm\(^3\), and additionally showed a high transparency and a breakdown voltage as high as conventional polyimide. Additionally, we hybridized the biopolymides with silica by sol-gel methods to get the increased insulating performed with keeping high transparency. The transparent biomaterials can be used for next-generation transparent and flexible materials.

Enroute Towards Biodegradable Organic Electronics Materials and Devices

Clara Santato1, Eduardo Di Mauro2 and Denis Rho2; 1Engineering Physics, Polytechnique Montreal, Montreal, Quebec, Canada; 2National Research Council Canada, Montreal, Quebec, Canada.

Electronics have become indispensable in our daily routine. A great part of the electronic equipment that surrounds us belongs to what is known as conventional electronics, based on inorganic materials such as silicon and gallium arsenide. However, with the life of the electric and electronic equipment becoming shorter and shorter, two major issues arise for both the scientific community and municipalities: the increasing amount of Waste of Electrical and Electronic Equipment (WEEE) and the depletion of natural resources. Taking into account the definition of sustainability provided by the United Nations (the ability of satisfying one generation’s needs without compromising the possibility of future generations to satisfy), those two issues point to the lack of sustainability in the electronics field of the current generation, at least so far. Consequently, great attention has been given to green (sustainable) electronics in the last years, having as core values (i) the use of abundant and low-cost precursors, leveraging on processing routes that (ii) lack toxic solvents as well as toxic waste and (iii) are low cost and (iv) involve biodegradable materials. In this contribution, we will present our preliminary results on the biodegradability and compostability of organic electronic materials of interest for electronics and energy storage devices, focusing on the case of study of melamin biopigments used in transistors, batteries and supercapacitors.

Fully Bioabsorbable Natural-Materials-Based Triboelectric Nanogenerators

Zhuo Liu1, Yubo Fan2 and Zhou Li2; 1School of Biological Science and Medical Engineering,
Implantable medical devices provide an effective therapeutic approach for neurological and cardiovascular diseases. With the development of transient electronics, a new power source with biocompatibility, controllability, and bioabsorbability becomes an urgent demand for medical sciences. Here, various fully bioabsorbable natural-materials-based triboelectric nanogenerators (BN-TENGs), in vivo, are developed. The triboelectric series of five natural materials is first ranked, providing a basic knowledge for materials selection and device design of the TENGs and other energy harvesters. Various triboelectric outputs of these natural materials are achieved by a single material and their pairwise combinations. The maximum output voltage, current, and power density reach up to 55 V, 0.6 μA, and 21.6 mW m⁻², respectively. The modification of silk fibroin encapsulation film makes the operation time of the BN-TENG tunable from days to weeks. After completing its function, the BN-TENG can be fully degraded and resorbed in Sprague–Dawley rats, which avoids a second operation and other side effects. Using the proposed BN-TENG as a voltage source, the beating rates of dysfunctional cardiomyocyte clusters are accelerated and the consistency of cell contraction is improved. This provides a new and valid solution to treat some heart diseases such as bradycardia and arrhythmia.

9:45 AM *EP03.04.04
Bioresorbable Electronics Based on Solvent Treatment Stabilizing the Room-Temperature Sintering Xian Huang, Hang Xu and Jianming Li; Biomedical Engineering, Tianjin University, Tianjin, China.

Bioresorbable electronics can be developed using various fabrication approaches that involve conventional CMOS fabrication following by transfer printing on bioresorbable substrates or printing techniques that demand high performance bioresorbable inks. Bioresorbable inks based on transient metal typically require high temperature sintering processes or photonic sintering that will lead to improvement in both electrical conductivity and mechanical strength. However, the resulting devices have not yet satisfied the requirement of high performance electronics and are mechanically weak to withstand large deformation. Here, new ink materials, electronics devices, and the concept of spontaneous room-temperature sintering will be presented. Environmental humidity or UV light treatment activate surface chemistry in the new ink materials, causing removal of surface oxidation of transient metal nanoparticles as well as intimate contact between neighboring particles. The highly conductive metal particle network and robust polymer binders ensure improved electrical conductivity and mechanical strength, leading to flexible devices that are presented as RFID circuits, passive components, and sensors. The new composition and processing techniques have minimum requirements to the temperature and environmental conditions, and offer effective solutions to mass fabricate bioresorbable electronics that can be potentially used in implantable monitoring, sensitive data storage, and consumer products.

9:55 AM *EP03.04.05
Biodegradable Elastomers for Stretchable Light-Emitting Electrochemical Cells Martin Held, Natalie Lam, Manuel Pietsch, Philip Hindenberg, Carlos Romero-Nieto and Gerardo Hernandez-Sosa; Light Technology Institute, Karlsruhe Institute of Technology, Heidelberg, Germany; Institute of Organic Chemistry, Heidelberg University, Heidelberg, Germany.

Achieving biodegradability in optoelectronic devices, such as light-emitting electrochemical cells (LECs), requires assessing every component for its degradability in a biologic environment. The substrate makes up the vast majority of the device’s mass, thus governs its biodegradability and mechanical behavior. While biodegradable thermoplastic foils provide mechanical flexibility by bending, they don’t offer any elastic stretchability. However, replacing biodegradable thermoplastics with elastomers would extend the range of potential applications in packaging and medicine. Silicone-based elastomers are frequently used as stretchable substrates but are merely biocompatible, not biodegradable. We present four different biodegradable options as elastic substrates for LECs with different processing concepts: A commercially available compostable thermoplastic elastomer (Terratek Flex), two synthesized poly(glycerol-sebacate) elastomers being either photo- or thermally cross-linked and a gelatin-blend from commercial ingredients. Their suitability as substrates is investigated by the optoelectronic performance of LECs. These are composed of biodegradable and biocompatible materials and fully printed via inkjet printing and doctor blading. Their charge transport and light-emission is characterized under increasing isotropic strain of the elastic substrate. The combination of stretchable biomaterials with up-scalable manufacturing techniques will enable the fabrication of transient and disposable electronic products ranging from biodegradable smart packaging via soft robotics to skin-adhered wearable healthcare applications, without adding to the global plastic carpet.


10:00 AM BREAK

10:30 AM *EP04.03.04
Solvent Treatment Stabilizes the In Vitro Response of Enzymatic Sensors Dongliang Wang; University of Connecticut, Storrs, Connecticut, United States.

Long-term stability of enzymatic devices present great challenges toward the realization of long-term implantable glucose sensors. Semi-permeable polyurethane (PU) membranes situated above the glucose oxidase enzyme, are typically used to balance the glucose to oxygen ratio and afford linearity over the entire physiological glucose range. Here is shown that the as cast PU membranes are prone to an initial swelling and subsequent densification that result in a large drift in sensor sensitivity over a period of 2 months. Exposing the PU-coated sensor to solvent vapors eliminates the aforementioned morphological changes. This eliminates the sensitivity drifts and provides exceptional, long-term, glucose sensor stability. The close zigzag packing of PU chains alongside the formation of ordered H-bonding that stabilizes and provides stable diffusion characteristics for such segmented PU membranes. The ability to maintain the stability provides a crucial advance in the fabrication of long-term enzymatic devices and implantable biosensors.

10:45 AM *EP04.03.04
Silicon Nanomembrane-Based Visible/Infrared Phototransistors and Their Applications in Transient Electronics Gongjin Li, Ruobing Pan, Enming Song, Qinglei Guo, Gaoshan Huang and Yong Feng Mei; Fudan University, Shanghai, China.

A remarkable superiority of silicon electronics is its biological affinity and excellent semiconductor processing property. Among various synthesized forms of silicon materials (e.g. bulk silicon, silicon quantum dots, silicon nanowires or tubes), silicon nanomembranes (Si-NMs) show great optoelectronic application potential due to its low flexural rigidity and self-assemble adaptability into novel 3D origami structures. The traditional strategies for Si-NMs based optoelectronic devices is a device-last process, which depends on releasing the Si-NMs by etching the buried oxide (BOX) layers of silicon-on-insulator (SOI) wafers and transfer it to the desired substrate with wet or dry processes.

We proposed flexible phototransistors and their multifunctional applications by the use of wafer-compatible Si-NMs synthesis strategy. This process is suitable for the transferring of continues large area nanomembrane in the wafer scale. An efficient gate modulation significantly restrains the dark current to 10⁻¹² A and yields an ultrahigh photo-to-dark current ratio of >10⁶ with a responsivity of 1.34 A/W. Based on the mechanism of surface plasmon polariton hot holes injection, we demonstrated that the spectrum response of Si-NM phototransistors can be tuned to near-infrared range (e.g. 1550 nm) by decorating the light-sensitive channel with nano groove gold arrays. Such high-sensitivity phototransistor could be applied in the application of biological sensors and biochips. Optoelectronic sensing of hydrogen concentration and environment humidity have been realized by decorating the top surface of phototransistor with certain sensitive materials.

To satisfy the requirements for the transient form of flexible electronics capable of working at high-temperature, Si-NMs electronics was integrated with a 4-μm thick high-temperature degradable (~300 °C) poly-α-methylstereine (PAMS) interlayer, which enables distinct and irreversible transient process for Si-NM devices. The function expandability of the Si-NM phototransistors as well as the wafer-compatible fabrication exhibit great potential for the sensing functions in the future portablewearable bio-friendly electronic integrating system with multifunctional applications.

Acknowledgement: This work is supported by the Natural Science Foundation of China (51711150298, U1632115 and 51602056), Science and Technology Commission of Shanghai Municipality (17JC1401700), the National Key Technologies R&D Program of China (2015ZX02012-003) and the Changjiang Young Scholars Program of China.

References:
The growing demand for implementing wearable and implantable devices that can sense and harvest energy from human motion and biomechanical vibrations, is motivated to build next-generation smart sensors, flexible circuits, and artificial electronic skin devices. Recently, triboelectric nanogenerator devices based on electrostatic induction have been demonstrated to scavenge mechanical vibrations. For the seamless interface between the devices and human tissue, it is required that the devices are composed of soft, flexible, and biocompatible materials. In addition, obtaining conductive electrodes for the bio-devices is still challenging due to the tradeoff between the flexibility and conductivity. Attractive properties of silk protein such as biocompatibility, flexibility in thin film form, compatibility with the aqueous solution, and highly optical transparency have made it to be a promising candidate for realizing wearable and implantable electronic devices. Herein, we present the fabrication of flexible, transparent, and biocompatible single-electrode silk bio-triboelectric nanogenerators (SBTENG) to sense and harvest energy from biomechanical vibrations. We constructed a SBTENG using a 0.12 mm thick silk film with the grating structure of periodicity of 1.5 μm and the buried silver nanowires (Ag-NWs) network with a sheet resistance of 35 Ω sq⁻¹. The fabricated SBTENG devices offer biocompatibility, flexibility and transparency (average transmittance of 85%) in the visible region, which are essential for bioelectronics. The SBTENG is capable of outputting an open circuit voltage of 90 V (V\text{max}) and the maximum power density of 2 mW/m² on a load of 1 MΩ under light finger tapping, which can drive five commercial green light emitting diodes instantaneously. The mechanism of SBTENG is based on the tribo-charge generation on the surface of silk upon tapping it with human finger. Owing to the transparency of the SBTENG devices, they can be attached to electronic devices (commercial cell phone and electrical mouse) to harvest the biomechanical energy with an output power of 1 μW. The low cost, ease of fabrication, biocompatibility, flexibility and transparency of SBTENG devices enable their potential usage in applications including human-machine interface, touch sensor, and biomechanical energy harvesting.

**SESSION EP03.05: Bioelectronic Interface**

**Session Chairs:** Hui Fang, Mihai Irimia-Vladu and Lan Yin

**Wednesday Afternoon, April 24, 2019**

**PCC North, 200 Level, Room 221 C**

**1:30 PM** **EP03.05.01**

**Hydrogel-Based Electronics—Ultracompliant Electrodes for Neural Interfaces and Beyond**

**Christopher J. Bettinger; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.**

Flexible electronic devices underpin many biomedical technologies that record and stimulate neuronal activity from organs in the central and peripheral nervous systems. Reliable and stable chronic recording from excitable tissues using implantable multielectrode arrays has been elusive to date due, in part, to host tissue interactions that contribute to device failure. Local tissue damage and device failure is worsened by the mechanical mismatch between materials used to fabricated rigid silicon-based microfabricated multielectrode arrays (E\text{HEA} ~ 100 GPa) and tissues in the nervous system (E\text{PNS} ~ 10 kPa). Hydrogel-based electronics could reduce the mechanical mismatch across the tissue-device interface and enhance performance. Furthermore, adhesive ultraflexible hydrogel-based electrodes have potential applications in wearable devices ranging from EEG electrodes to consumer electronics. Here we present materials and companion fabrication strategies to create ultraminiaturized electronic devices for use in peripheral nerve interfaces. Integrated strategies for polymer synthesis, processing, and microfabrication are described. Details regarding the in vitro and in vivo performance of these devices will also be presented.

**2:00 PM** **EP03.05.02**

**Biologically Produced Fluorescent Proteins for Advanced Photonic Devices**

**Malte C. Gather; School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.**

Organic materials offer attractive properties for solid-state lasers, including large oscillator strength, high exciton binding energy, spectral tunability, and compatibility with low-cost fabrication processes. However, despite impressive proof-of-principle demonstrations and dramatic improvements in performance, important fundamental limitations remain. Particular challenges are concentration quenching and bi-molecular exciton recombination which limit the available gain under practical pumping conditions. Here, I will summarize key results from a number of studies that we performed on a rather unconventional class of organic materials, the biologically produced fluorescent proteins. The nano-scale barrel-like molecular structure of fluorescent proteins like GFP prevents concentration-induced quenching of fluorescence and drastically reduces singlet-singlet annihilation at high exciton densities. This facilitates low-threshold lasing in various configurations and has recently enabled the realization of the first organic polariton laser that can be pumped in a quasi-continuous ns-regime.

**2:15 PM** **EP03.05.03**

**Photothermally Tunable Biodegradation of Implantable Triboelectric Nanogenerators for Tissue Repairing**

**Zhe Li and Zhou Li; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.**

Implantable triboelectric nanogenerators (iTENGs) are promising to work as sustainable power source for implanted healthcare electronic devices. In this study, we fabricated a serial of biodegradable (BD) iTENGs and effectively tuned their degradation process in vivo by employing Au nanorods (AuNRs), which responded to the near-infrared (NIR) light sensitively. The implanted BD-iTENG worked well for more than 28 days in vivo, without NIR treatment. When NIR treatment was applied, the output of AuNRs-BD-iTENG rapidly reduced to 0 within 24 h and the device was mostly degraded in 14 days. This showed that the in vivo degradation of our BD iTENG could be triggered and come into effect very quickly with rational manipulation. The peak value of in vitro and in vivo output voltage generated by the AuNRs-BD-iTENG were 28 V and 2 V, respectively. Moreover, the in vivo output voltage was applied on fibroblast cells and demonstrated a significant acceleration for cell migration across the scratch, which was very beneficial to wound healing process. In addition, we discovered that the alternating BD-iTENG output was as efficient as direct current (DC) stimuli. The mechanisms were investigated. Our work has demonstrated the feasibility of building a photothermally tunable BD-iTENG as a transient power source for biomedical healthcare electronics.

**2:30 PM BREAK**

**3:30 PM** **EP03.05.04**

**Biomimetic and Bioactive Strategies Towards Seamless Neural Implants/Tissue Integration**

**Tracy Cui; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.**

Microelectronic devices placed in the nervous system present tremendous potentials for investigating neural circuits and treating neurological disorders. Currently, these devices often experience failures in part due to the electrical, mechanical, and biochemical, mismatch between the artificial device and neural tissue. Quantitative histology and 2 photon imaging have revealed neuronal damage and degeneration, inflammatory gliosis, blood brain barrier leakage and oxidative stress as a result of implantation. Several biomaterial strategies have been investigated to minimize the mismatches and achieve seamless and stable device-tissue interface. First, various conducting polymer based nanocomposites have been investigated as electrode coatings and facilitate the signal transduction/charge transfer between ionically conductive tissue and electrical device. Secondly, to minimize the mechanical mismatch at the device-brain tissue interface, novel soft and elastomeric electrode materials have been developed with Young’s modulus approaching that of neural tissue (less than 1 MPa). Soft implants demonstrated reduced inflammatory tissue response in both CNS and PNS compared to stiff implants of similar geometry and surface
All Organic Piezoelectric E-Skin Sensor for Self-Powered Wearable Electronics and Human Physiological Signal Monitoring

**Kuntal Maity** and Dipankar Mandal

4:00 PM EP03.05.05

Rapid developments of smart electronics, flexible and wearable e-skin sensors are attracting a great deal of attention due to their smart sensing applications in next-generation devices. Interestingly, it can eventually measure and quantify electrical output signals generated by various human activities.[1,2] However, the flexibility, biocompatibility, sensing capability, cost-effectiveness and packaging are the main concerns, which immensely drive to carry out this present work.[3,4] In this framework, organic piezoelectric materials such as poly(vinylidene fluoride) (PVDF) and its copolymers are of particular interest towards device integration, having adequate advantages over inorganic materials.[5,6] In addition, it should be mentioned that the choice of electrodes and their compatibility with organic and hydrophobic surfaces of PVDF remain challenging tasks, particularly when device performance, durability and implant ability are concerned. The brittleness, toxicity and high cost of inorganic materials have prohibited its use as a conducting electrode; in addition, direct adherence on electrospun nanofibers (NFs) surface is one of the major challenges to build the permanent electrodes in device structures. In contrast, organic conducting polymers are being presented as a viable alternative for organic electronic device, particularly if one can achieve adequate coating on the electrospun polymer fibers.[7]

Here we present an all-organic piezoelectric e-skin sensor (AOPESS) based on highly aligned poly(vinylidene fluoride) (PVDF) NF arrays and conducting polymer i.e. polyaniline (PANI) coated PVDF NFs mat as electrode; for energy harvesting from various types of mechanical motions and self-powered human physiological signal sensing. The electropinning technique in combination with vapor phase polymerization (VPP) enables such aligned structure followed by successive coating of PANI upon PVDF NFs surface. The Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and Field emission scanning electron microscope (FE-SEM) clearly indicate the successful coating of PANI upon the PVDF NFs surface. The electrical performances were clarified by measuring the current-voltage (I-V) characteristic under the application of external pressure. Owing to highly aligned structure with superior piezoelectric β-phase contained (~98%) and excellent electrode contact-adherence, AOPESS exhibits a effective conversion of mechanical energy of human finger movements into electrical energy (~10 V). The coating of PANI upon PVDF NFs opens the use of organic electrode in various applications especially for e-skin devices solving the so called electrode issues. Recently, human physiological signal monitoring is an effective approach for the assessment of various human health problems. So, we can monitor our physiological signals such as body temperature and heartbeat rates.[8,9] More importantly AOPESS can show ultra-sensitivity towards various human movements such as wrist bending, neck stretching, arm compressions, throat movement, and phonation recognition to name a few. Thus it will play an essential role in future wearable electronics and shed light on multiple advancements like electronic skins to human–machine interfaces.

References


4:15 PM *EP03.05.06

**Tattoo Paper as a Platform for Bio-Friendly and Skin-Contact Conformable Electronics**

Francesco Greco;

1 Institute of Solid State Physics, Graz University of Technology, Graz, Austria; 2 Center for Micro-BioRobotics, Istituto Italiano di Tecnologia, Pontedera, Italy; 3 Department of Life Science and Medical Bioscience, Waseda University, Tokyo, Japan.

The combination of conformable and organic bioelectronics can enable a full range of unprecedented applications, from perceivable personal monitoring systems -to- be used in healthcare and sport, especially in skin contact applications- to bio-friendly and edible electronics.

To this aim we chose Temporary Tattoo paper as an unconventional substrate for developing ultra-thin and transferrable devices which are able to conform to surfaces with complex topography. Such a layered material is composed of (i) a support paper, (ii) a water-soluble starch/dextrin sacrificial layer, and (iii) a releasable ethylcellulose nanosheet (thickness ~ 500 nm). It is commercially available in the form of large area sheets or rolls at very low cost.

In a first part of this talk I will report about a robust, low cost and safe strategy for producing disposable ultraconformable electrodes for skin-contact electrophysiology recordings. Temporary Tattoo Electrodes (TTE) and multielectrode arrays (TTMEA) based on conducting polymer PEDOT:PSS are fabricated by ink-jet printing, laser cutting/engraving and lamination. Thanks to this choice, several different configurations of arrays can be customized for different applications. They can be transferred on skin as temporary transfer tattoos and the overall thickness of such electrodes is < 1 μm. We demonstrated their successful performances as stable, dry electrodes for several electrophysiological recordings: skin impedance, surface electromyography (sEMG) on limbs and face, electrocardiography (EKG), and the most challenging electroencephalography (EEG). TTEs demonstrated stable adhesion and operation on skin. Long-term recording was assessed which favorably compares with state of art Ag/AgCl electrodes. Moreover myographic control of a robotic hand through TTE was demonstrated paving the way to novel applications as perceivable sensors in human and brain machine interfaces.

Temporary Tattoo-paper is furthermore proposed as a simple and versatile platform for the integration of electronics onto food and pharmaceutical capsules. In particular, the fabrication of all-printed organic field-effect transistors on untreated commercial tattoo-paper, and their subsequent transfer and operation on edible substrates with a complex nonplanar geometry is demonstrated.

References


4:45 PM EP03.05.07

**Conductive Polyhydroxybutyrate/Reduced Graphene Oxide Biocomposite Temperature Sensor**

Dan Li and Anastasia L. Elias; Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada.

As wearable devices gain traction, inexpensive and simple sensors that can connect with an internet of things platform are promising devices for continuous wellness data monitoring. One approach to making such sensors is using stimulus-responsive (i.e. smart) materials. Inspired by nature, smart materials sense a stimulus in their surroundings and undergo a measurable change in property. Smart materials based on nanoparticle- polymer composites can be designed to sense various stimuli and exhibit changes in color, resistance, capacitance, etc. In our composite systems, conducting nanoparticles (carbon-based materials) impart electrical conductivity to the composite, while the bio-compatible and bio-derived polymer matrix provides mechanical stability. Either the polymer or the nanofiller (or both) may act as the sensing element, undergoing changes in electronic properties in response to an external stimulus. In this presentation, a negative temperature coefficient (NTC) temperature-sensitive composite is reported (where the NTC is defined as (R-R0)/R0△T). Our materials consist of a high melting point biopolymer (polyhydroxybutyrate (PHB)) and graphenic nanomaterial (reduced graphene oxide (rGO)). At a given temperature, the electronic properties of the composites are strongly dependent on the concentration of rGO within the polymer matrix. Upon heating, these materials exhibit large and reversible changes in resistivity (NTC of ~ 0.08°C and fast response time (less than 70 ms for a 3 wt% rGO composite). This response results from the semiconducting properties of the rGO where the number of charge carriers in the conduction band increases with temperature, thereby reducing the overall resistivity of the composites. These responsive conductive composites are good candidate for low-cost sensing devices. The composites are solution processable and thus are compatible with many printing techniques such as direct printing. Devices are capable of measuring dynamic change of temperature subjects with curved surfaces and of thermomapping a large area. Devices are further connected to the wireless system to monitor wellness data in a time-controlled manner.
Facile Non-Invasive Electrical Probe for Studying Photoinduced Events in Primary Explants C.S. Deepak, Sumukh Purohit, Anil Krishna Konduri and K.S. Narayan; School of Advanced Materials (SAMAT) and Neuroscience Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore, India.

Quantitative assessment involving non-contact electrical methods without the involvement of microscopy can enable a remote user to monitor the cell growth and development at different stages. We introduce and demonstrate a facile approach to probe the ensemble of cells and the role of environment and substrates in the growth and functions. Specifically, cell lines which are of neuronal like and primary explant from chick-embryo retina are studied closely using this novel monitoring method along with conventional from multielectrode array (MEA) type electrical recording approaches. The studies using this technique of the cells at different stages of growth and the changes introduced upon differentiation point to the versatility of the approach. The environment of the cells are varied by choice of different substrates including a variety of non-rigid substrates with different degrees of electrical properties. Optoelectronic substrates with the ability to absorb light and change the surface potential to trigger stimulated responses from the cells and blind-retina explants are also demonstrated. A specially designed microfluidic setup which eliminates air bubbles and is integrated to the measurement assembly was developed to carry out long-term recordings. A systematic development studies of chick retina from the blind-stage (day 12) to a fully mature state (day 21) was carried out. We utilize this chick-model system to study the signal transduction mechanism and pathways upon introducing artificial photoreceptors.

Organic Electrochemical Transistor Response to Liquid and Solid Bacteria Growth Media Eric Frantz, Ashkan Tirgar and Andrew J. Steckl; University of Cincinnati, Cincinnati, Ohio, United States.

Ion generation in bacteria cells is a central component in their life cycle. Ion generation helps us understand bacterial responses to stimuli, as well as the mechanisms by which ion transport is regulated. Recent attention has been given to ion-based communication within and between bacteria colonies [1]. Two methods of detecting bacterial ions are fluorescent and electronic detection. Fluorescent dyes provide a view of ion concentrations spatially, allowing detection of ion movement and position both within and outside cells. Electronic measurements are limited to extracellular ion concentrations and are typically performed using ion selective electrodes (ISEs) or ion-selective FETs (ISFET) to measure specific ion concentrations or changes in pH. We report on the use of organic electrochemical transistors (OECTs) to sense ion concentrations in bacteria growth media. OECTs high transconductance, bio-compatibility, low cost, and small size have made them a popular sensor for detection and characterization of whole cells [2]. OECT switching is driven by ions from either a liquid or solid source. Understanding changes in OECT behavior for different solid and liquid ion sources is needed to fully optimize device for specific applications. These changes can come from ion concentration and species (or other particulates) and significantly affect device operation. Cells captured or cultured onto OECTs can induce a change in effective gate voltage, or a change in transconductance due to their effect on medium pH. While the OECT response to the presence of various cells has been reported, the effect of the culture medium has not been reported. Characterization of the driving electrolyte, or culture medium, is needed to optimize OECT performance and sensitivity for whole cell detection. We have tested transconductance, ON/OFF ratio, and peak transconductance gate voltage of PEDOT:PSS based OECTs operating in several media: KCl, NaCl, PBS, LB broth, YT broth, and water solutions. Our results show peak device transconductance utilizing 0.1M KCl, which is in line with literature [3]. A decrease of 37.7 μs (57%) and 55.1 μs (84%) is shown for LB and YT culture media compared to the 0.1M KCl solution. An increase in ON/OFF ratio of LB and YT broth of 300% and 224% is obtained, compared to 0.1M KCl solution. Interestingly, a reduction in peak transconductance gate voltage from −0.6V to −0.3V was measured for both broth solutions compared to pure electrolyte solutions (KCl, NaCl, etc.). This is beneficial for operating under low OECT power conditions. Overall, these results indicate that cell culture media play an important role in OECT-cell interactions.


Organic Electronic Devices as Multi-Modal Transducers of Cellular Activity Roisin Owens and Charalampos Pitsalidis; Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, United Kingdom.

In vitro models of biological systems are essential for our understanding of biological systems. In many cases where animal models have failed to translate to useful data for human diseases, physiologically relevant in vitro models can bridge the gap. Many difficulties exist in interfacing complex, 3D models with sensing technology adapted for monitoring function of cells within these models. Polymeric electroactive materials and devices can bridge the gap between hard inflexible materials used for physical transducers and soft, compliant biological tissues. An additional advantage of these electronic materials is their flexibility for processing and fabrication in a wide range of formats. In this presentation, I will discuss our recent progress in adapting conducting polymer devices, including simple electrodes and transistors, to integrate with 3D cell models. We go further, by generating 3D electroactive scaffolds capable of hosting and monitoring cells. In some cases, it is useful to zoom in on interactions occurring at the molecular level, to read out events happening at the level of the cell membrane. In addition to monitoring properties of cells and tissues, electrical monitoring is a powerful tool to monitor transmembrane protein function. I will highlight recent research using biomimetic models of cell membranes interfaced with organic electronic devices for drug discovery.

Electrolyte-Gated Carbon Nanotubes Transistors for Electrical Monitoring of Cell Cultures Francesca Scarratti1,2, Giorgio Bonacchini1,2, Caterina Bossio1, Jorge Mario Salazar-Roos1, Wytse Talsma1, Maria Antonietta Loi1, Maria Rosa Antognazza1 and Mario Carrelli1; Istituto Italiano di Tecnologia, Milano, Italy; Politecnico di Milano, Milano, Italy; University of Groningen, Groningen, Netherlands.

Solution-processed, carbon based electrolyte-gated transistors represent an ideal ionic/electronic hybrid device that bridges biology and electronics. These devices are being investigated for a wide range of applications, from drug delivery to neuromodulation and highly sensitive biosensing. Cell-based electrical bio-sensors are of particular interest because they can enable a high level of automation and parallelization in real-time in vitro monitoring of cells cultures, highly desirable for dianostics and toxicology tests. While typical sensing platforms rely on impedance measurements, we propose here an electrolyte-gated transistor for cell viability monitoring, based on a network of solution-processed, polymer-wrapped semiconducting carbon-nonotubes. Our sensors display extended stability to water-gating and allow an easy signal read-out, without requiring complex modeling and/or parameters fitting, as this corresponds to variations in the static transistor channel current. We demonstrate successful cell-proliferation monitoring in excess of 70 h of three different cell models.

10:00 AM BREAK

Light-Responsive Materials for Bioelectronics from Photosynthetic Microorganisms Gianluca M. Farinola1, Massimo Trotta2, Roberta Ragni1, Francesco Milano2, Angela
Photonsynthetic microorganisms can be envisaged as sources of active materials for bioelectronic devices for photocconversion or light-induced processes. In particular, photosynthetic Reaction Centers (RCs) are enzymes capable to convert solar energy into charge separated states with efficiency close to 100%. We have first reported the highly selective covalent functionalization of the bacterial RC with several classes of tailored molecular fluorophores which act as antennas to enhance its light harvesting capability. The resulting hybrid systems outperform the native protein in the photogeneration of charges and in the photoenzymatic activity. We have also built up smart supramolecular architectures combining multiple enzymes assembled with tailored linkers, which are able to perform manifold functions. Finally, we have developed protocols for addressing the RC on thin films of molecular or polymeric semiconductors deposited onto metal electrodes by covalent or weak collective interactions, obtaining RC-sensitized electronic and electrochemical devices. Biomimetic polymers, such as polydopamine mimics of melanin, have also been investigated as efficient electronic interfaces of RC with electrodes in photoelectrochemical cells.

Our study discloses new concepts for the generation of bio-hybrid materials for sunlight photocconversion and for light-triggered bioelectronics, by combination of tailored functional molecules with highly efficient photo-active natural structures optimized in billions of years of evolution.

References

11:00 AM EP03.06.06 Conductive Biopolymeric Proteins for Bio-Hybrid Devices Noemie-Manuelle Dorval Courchesne; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Using proteins as active device components is of particular interest for the fabrication of next-generation electronic devices. Proteins provide soft, biocompatible and genetically tunable surfaces that can be rationally engineered to participate in charge transport processes. In addition, proteins can retain biological functions, to produce multifunctional bioelectronics materials that could be applied to a variety of bio-sensing and bio-energy applications. Here, we report the fabrication of conductive protein gels and films with novel opto-electronic properties. We fabricated these protein-based materials using genetically engineered amyloid proteins as building blocks and introduced desired functionalities via synthetic biology. Using bio-inspired and bio-derived syntheses, we have developed strategies to produce and isolate macroscopic quantities of functional protein materials. We have explored the synthesis of electronically conductive protein fibers and films, by introducing aromatic residues within the core of the self-assembling amyloid proteins. We have characterized the electrical properties of these proteins, and examined factors that influence the conductivity in such protein systems. In addition, we are investigating the potential of engineered proteins to participate in light harvesting in bio-hybrid energy devices. Our scalable biosynthesis process allows us to produce engineered protein materials in sufficient quantities to integrate them, in the future, in bio-hybrid functional devices.

11:15 AM EP03.06.07 Perovskite Biointerface for Optical Stimulation of Neuronal Cells Shashi B. Srivastava1, Mohammad M. Aria2, Emine Sekerdag2, Ugrur M. Dikbas2, Sadra Sadeghi2, Samuel Pering2, Petra J. Cameron3, Yasemin Gursoy-Ozdemir4, 1Ibrahim H. Kavakli5 and Sedat Nizamoglu6-2 1Electrical and Electronics Engineering, Koc University, Sariyer, Turkey; 2Graduate School of Biomedical Sciences and Engineering, Koc University, Sariyer, Turkey; 3Molecular Biology and Genetics, College of Science, Koc University, Sariyer, Turkey; 4Neuroscience Research Lab, Research Center for Translational Medicine, Koc University, Sariyer, Turkey; 5Graduate School of Materials Science and Engineering, Koc University, Sariyer, Turkey; 6Department of Chemistry, University of Bath, Bath, United Kingdom; 7Department of Neurology, School of Medicine, Koc University, Sariyer, Turkey; 8College of Engineering, Chemical and Biological Engineering, Koc University, Sariyer, Turkey.

Organometallic halide perovskites are fast grown photocative material in the field of solar cell technology due to high absorption coefficient, almost 100 % internal quantum efficiency, high diffusion length, and broader absorption wavelength (visible to near IR spectrum) [1,2]. Their advantageous optical properties provide high potential to use perovskites as biointerface. But, low stability in aqueous environments and the presence of toxic lead content in commonly used perovskite semiconductors make it difficult to use in the biological environment. Although there is significant focus on lead-free perovskites, their performance remained far from the lead-based perovskites. In order to use perovskites as photodetector for neuronal prostheses, three important conditions including stability in water, biocompatibility, and generation of safe photostimulation need to be satisfied. The present work demonstrates the first use of perovskite for neural interfaces. The photodetector consist of a perovskite photocoactive layer sandwiched between transparent conducting oxide (ITO-Indium tin oxide) and biocompatible PDMS (dimethylpolysiloxane, a silicon-based organic polymer):P3HT (Poly(3-hexylthiophene), a semiconducting polymer) hybrid layer. The coverage of PDMS layer over perovskite thin film blocks the direct contact of neuron cells with toxic perovskite for biocompatibility. It also functions as an encapsulant against water that lead to enhanced stability in aqueous medium. Furthermore, we observed that the thickness of the perovskite layer is critical to generate safe capacitive photostimulation. We studied the perovskite biointerface with ShSy-5Y neuronal cells using whole-cell patch clamping and observed depolarization of the cells.

References
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Blood is the most intensely studied human biofluid and is used as the main indicator (so-called “gold standard”) of the health status of the individual. Blood is a biologically renewing fluid with ~1 million red blood cells (RBCs) injected every second from the bone marrow into the blood stream (equivalent to ~10^11 RBCs being created every day) of an adult human body and a similar number cleared or recycled. Blood is a very complex fluid, containing a multiplicity of components, including cells and cell fragments (red and white blood cells, platelets), proteins, and many other organic molecules and ions. Laboratory-based blood analysis is a well-established procedure that provides a wealth of information about the concentrations of key blood components and enables medical personnel to establish diagnoses and treatments. It is typically performed in hospital or laboratory settings using a variety of methods and equipment, with the emphasis on accuracy and measurement automation. To date, options for point-of-care blood analysis are limited and very low-cost options even more so. One analytical platform that contains the promise to fill this need utilizes cellulose-based microfluidic devices. Cellulose, the most abundant naturally occurring organic compound (polysaccharide), is the main constituent of cell walls in plants and is available in many practical forms, including conventional paper. Paper microfluidics utilizes the self-wicking ability of paper by capillary action to implement simple device that do need external pressure to transport fluids. This has opened the door to simple paper-based point-of-care (PoC) or point-of-use (PoU) devices for monitoring various medical conditions (e.g. pregnancy testing, virus assays, etc.). This research area has exhibited significant growth in the past few years, primarily because of its simplicity, fundamental low cost, and versatility. This presentation provides a review of several important applications, including blood grouping, glucose and coagulation monitoring, biomarker detection. The presentation concludes with a discussion of current challenges of paper-based blood diagnostics and a look forward to future prospects.

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Aqueous Electrolyte Compatible Electrochromic Polymers Processed from Environmentally Sustainable Solvents
Graham Collier, Ian Pelse, Anna Osterholm and John Reynolds; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.
Developing aqueous electrolyte compatible, redox-active polymers that can be processed from environmentally sustainable solvents is desirable because these traits will effectively reduce environmental impact and human health hazards during processing procedures and in the final device architecture. Additionally, the ability to dope and dedope conjugated polymers in aqueous media may allow for conjugated polymers to find applicability in biological systems. In an effort to address these criteria, we have synthesized two ester-functionalized 3,4-propylenedioxy-thiophene polymers that are sufficiently soluble in environmentally sustainable (2-methyltetrahydrofuran) and benign (ethyl and propyl acetate) solvents to allow for processing as thin, electroactive films. Moreover, as the ester-functionality on the side chains is increased, the polymer films are able to be reversibly switched in aqueous electrolytes. The polymers were studied as electrochromic films as a case study and it was revealed that optical, electrochemical, and morphological properties showed slight variations depending on the casting solvent. However, properties such as switching time and contrast were unaffected. Our work highlights a simple design strategy to synthesize aqueous electrolyte compatible electrochromic polymers processable from sustainable solvents without post-polymerization modifications, which will ultimately reduce the environmental impact of electrochromic device fabrication and testing.

Helix-Rich Silk Fibroin Thin Films for Biocompatible Memory Devices
Mohammad Tahiib Sharbat, Se Youn Cho, Qionghou Wan, Golnaz Najafl Tomarazi, Nolan D Ardolino, Joshua Schleu, Mostafa Bedewy and Feng Xiong; University of Cincinnati, Cincinnati, Ohio, United States.
Silk fibroin produced by Bombyx mori silkworm, a fibroin protein-based biopolymer, has been used as a material for high-quality clothing since ancient times due to its superior textile properties such as lightness, fineness, and a unique luster. Moreover, because of its excellent strength and attractive biological properties, regenerated silk fibroin has been widely studied as a biomaterial over the past decades. Recently, silk fibroin has been considered as a promising candidate for biocompatible and green electronics due to its interesting resistive switching behavior. However, while prior works demonstrated promising proof-of-concept resistive switching, the high programming voltage, subpar on/off ratio, and limited endurance have hindered the development for silk-based resistive memory devices.
In this work, we present a comprehensive study to investigate how we may improve the electrical switching properties of silk memory devices by tuning its crystalline structure. First, as an initial effort, we fabricated 60+ devices and compared them with 20 of similar fibroin films that were able to be reversibly switched in aqueous electrolytes. The polymers were studied as electrochromic devices as a case study and it was revealed that optical, electrochemical, and morphological properties showed slight variations depending on the casting solvent. However, properties such as switching time and contrast were unaffected. Our work highlights a simple design strategy to synthesize aqueous electrolyte compatible electrochromic polymers processable from sustainable solvents without post-polymerization modifications, which will ultimately reduce the environmental impact of electrochromic device fabrication and testing.

Helix-Rich Silk Fibroin Thin Films for Biocompatible Memory Devices
Mohammad Tahiib Sharbat, Se Youn Cho, Qionghou Wan, Golnaz Najafl Tomarazi, Nolan D Ardolino, Joshua Schleu, Mostafa Bedewy and Feng Xiong; University of Cincinnati, Cincinnati, Ohio, United States.
Multi-Functional Nanocomposites from Naturally Derived Materials—Crystalline Celluloses and Conductive Melanin

Bong Sup Shim, Taesik Eom, Kyeonga Her and Seunghyeon Lee; Chemical Engineering, Inha University, Incheon, Korea (the Republic of).

Natural systems utilize multifunctional biocomposites by a bottom-up self-assembly of nanomaterials for creating multiscale, hierarchical, and multiphasic structures. While conventional man-made synthetic composites increase one functionality by sacrificing the others, the biocomposites often synergistically utilize their multi-functionalities. Here, by molecularly organized layer-by-layer assembly as well as thermodynamically driven orientation, we introduce multifunctional nanocomposites, recently developed from our laboratory, from natural biocomposites including high crystalline cellulose nanofibers and conductive melanin nanoparticles. High crystalline cellulose nanofibers, extracted from tunicates, have shown almost perfect crystallinity, straight fibrous shape, and liquid crystalline alignments. Thus, their nanocomposites showed uniquely oriented structures as well as excellent optical, mechanical, and barrier properties. On the other hand, naturally derived melanin nanoparticles are molecularly structured to possess finely tunable electrochemical conductivities, optical reflectivity, and casting shape stability with inherent biocompatibility. These composites can be used as key functional materials in the emerging applications such as biotic-abiotic smart interfaces, implantable electronics, and eco-electronics.

Photophysical and (Opto)Electronic Properties of Fungi-Derived Pigments and Their Polymer Blends

Gregory Giesbers, Jonathan Van Schenck, Sarath Vega Gutierrez, Rachel Van Court, Seri Robinson and Oksana Ostoverykhova; Oregon State University, Corvallis, Oregon, United States.

Organic semiconductors are of interest for optoelectronic applications due to their low cost, solution processability, and tunable properties. Recently, naturally product-derived organic pigments attracted attention due to their extraordinary environmental stability and unexpectedly good optoelectronic performance, in spite of only partially conjugated molecular structure. We present a study of the optical and electronic properties of several fungi-derived pigments and of their use in organic (opto)electronic devices. Fungi-derived pigments are a naturally sourced, sustainable class of materials that are yet to be explored as organic semiconductor materials. Examples of such pigments under study are a blue-green pigment xylindelmin, which is secreted by the wood-staining fungi Chlorociboria (C.) aeruginosa and C. aeruginascens, red pigment draconicin derived from Scytalidium cuboidenum, and a yellow pigment derived from Scytalidium ganodermorphthorum.

Photophysics of pigments is explored using absorption and photoluminescence (PL) spectroscopy combined with density functional theory calculations. In xylindelin and the red pigment (a novel naphthoquinone derivative), our studies reveal contributions of several tautomers to the optical properties and solvent-dependent pigment aggregation and crystallization. Molecular packing-dependent properties of aggregates and crystals were studied using polarization- and temperature-dependent absorption and PL and related to film or crystal structure and morphology obtained from the SEM and XRD. Photostability and thermal stability of pigments was also quantified.

(Opto)electronic properties of pristine pigments and their blends with synthetic polymers and naturally derived biopolymers, developed to improve film morphology and processability, were explored in several device structures. Charge carrier mobilities were obtained from space-charge limited currents and from measurements of thin film transistor characteristics and related to film structure and morphology. Some blends such as xylindelin:PMMA revealed ambipolar charge transport with charge carrier mobilities of up to ~0.01 cm²/Vs. Photoresponse was observed throughout the pigment absorption range, and photocurrent spectroscopy was carried out to obtain wavelength-dependent charge generation efficiencies. Charge and energy transfer in donor-acceptor combinations of pigments with several benchmark donors such as P3HT and PTB7-Th and acceptors such as PCBM were also investigated to determine the feasibility of using pigments under study in bulk heterojunction solar cells.

Directly Written Digital Microfluidic Systems for Ion Sensing Applications

Xin Min, Chao Rao and Woo Soo Kim; School of Mechatronic Systems Engineering, Simon Fraser University, Surrey, British Columbia, Canada.

Digital Microfluidic (DMF) devices have been developed recently as its promising ability to replace conventional laboratory processes. Small sample consumption and high controllability make the device suitable for electrochemical or biochemical applications. However, the fabrication of current DMF device is limited to rigid substrates, which confine its potential on flexible, fabric substrates for further applications. Here, we present DMF devices fabricated through additive manufacturing method with integrated on-chip ion-selective test function. The DMF electrodes are printed directly with conductive silver ink, followed by spin coating and spray coating of dielectric and hydrophobic layers. The overall fabrication procedure is easy and fast, which can be applied to various substrates. In addition, a capacitance monitoring system has been added to the device to obtain the droplet position and speed data in real-time for providing feedback signals. The ion-selective function is tested with a layer of ion-selective membrane on one of DMF electrodes. Fabricated DMF device demonstrated droplet manipulation functions including moving, mixing, and testing sequence. The on-chip membrane shows targeted ion selectivity from the droplet containing mixed interference ions.

Biofriendly Ionic Electromechanically Active Polymer Actuators

Fred Elhi, Pille Rinne, Karl Karu, Tarmo Tamm, Urmass Johanson, Vladislav Ivanistsev, Alvo Aabloo and Kaiaa Pohako-Esko; University of Tartu, Tartu, Estonia.

Electromechanically active materials change their shape under external electrical stimulation or generate electrical signal upon mechanical stimulus. These materials are in the focus of intense research as bioinspired devices need replacement for traditional actuators.

The present study aims to development of biofriendly ionic electromechanically active polymer actuators (IEAPs). A typical IEAP is a soft thin laminate composed of a microporous ion-permeable polymer membrane containing electrolyte (for example ionic liquid (IL)) placed between electrodes with a high specific surface area (for example conductive polymers). IEAPs can work as actuators and sensors transducing between electric current and mechanical deformation. In addition, IEAPs can sense temperature, humidity and chemical composition of the environment. Migration of ions in response to electrical stimulation enables controlled release. Combining all these functionalities leads to smart devices, which sense surroundings and react accordingly. Potential applications for IEAPs include implantable or disposable biomedical devices, smart prostheses, soft haptic devices and wearable electronics. Mentioned applications require biocompatible materials, which has still remained challenging during decades of research in the field.
Our approach towards biofriendly of IEAPs was to use biocompatible materials for different parts of IEAPs without compromising in performance. A key component hereby was low-toxicity IL as electrolyte. For electrode material polypropylene (PPy) was chosen due to proven biocompatibility: PPy is a suitable substrate for cell growth, implantable and can be functionalized to be biodegradable. Medically approved synthetic polymer PVDF and inherently biofriendly and biodegradable gelatin were applied and compared as membrane materials. So far mostly the conventional imidazolium based ILs had been used as electrolytes in IEAPs despite the well-known toxicological issues of these salts and a large variety of alternative ILs available. In the present study low-toxicity choline based ILs were applied instead.

In the presentation preparation, characterization, and electrochemomechanical performance of the developed biocompatible IEAPs will be discussed. Significant differences in actuation were found in case of different ILs as electrolytes although the actuators were found to be cation active and all of the ILs contained the same choline cation. Experimental results were explained using computational methods: formation of ionic clusters was studied with molecular dynamics (MD) simulations and with density functional theory (DFT) calculations.

8:15 AM EP03.09.02
Application of Biodegradable Polymers in Design of Green Printed Circuit Boards Reihaneh Jamshidi and Reza Montazami; University of Hartford, West Hartford, Connecticut, United States; Mechanical Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

Owing to the burgeoning waste electrical and electronic equipment is the effort to recycle the printed circuit board (PCB), which if improperly disposed of results in health hazards and environmental pollution. This study describes a new PCB substrate that would vanish in water leaving the metals on it for re-use. A preliminary substrate made from water, gelatin, and poly vinyl alcohol was coated with polyurethane for the purpose of preservation under humid conditions and a voltage divider circuit was attached. Dynamic mechanical analysis and thermomechanical analysis were performed to characterize the PCB for its physical characteristics, while Fourier transformed infrared spectroscopy was used for chemical characterization. It was demonstrated that the metal components including solder, copper, and electronic components can be fully recovered without generation of any toxic byproducts or negative impact on the environment.

8:30 AM EP03.09.03
Biodegradation of Organic Semiconductor Materials Luis F. Baptista, Natalia González, María del Carmen Molina, Carolina Vargas and Raquel Simarro; Department of Biology and Geology, Physics and Inorganic Chemistry, Rey Juan Carlos University, Mostoles, Spain; Department of Chemical and Environmental Technology, Rey Juan Carlos University, Mostoles, Spain.

Nowadays, the demand for electronic devices is exponentially increasing in our society. This fact, together with a shortening in their life cycle drive the depletion of non-renewable resources and the production of huge amounts of highly polluting electronic wastes. This is environmentally unsustainable at medium and specially at long term. Organic semiconductors arises as a promising alternative to traditional inorganic-based semiconductors for the fabrication of electronic circuits and devices. Besides other technological strengths, organic semiconductor devices can be designed to allow its biodegradation to avoid the pollution problem of traditional inorganic-based electronic devices. Therefore, the assessment of biodegradability of individual components of the electronic circuits and of the whole fabricated devices is a key issue for the future development of this environmentally friendly technology.

In the present work, efficient biodegradation processes for epindolidione, quinacridone and 2,8-difluoroepindolidione have been developed using different microorganism and microbial consortia under aerobic and anaerobic conditions. With respect to the biodegradation of epindolidione, among all tested bacteria, Stenotrophomonas sp. showed largest growth whilst the best microbial consortium capable live in that medium was the one isolated form Tinto river (South-West of Spain). We observed that during the first 21 days, the biodegradation was almost negligible for both Stenotrophomonas and for Tinto river consortium. However, at 73 days, the uptake of epindolidione with the consortium reached approximately 40% and 60% with Stenotrophomonas. After 100 days, epindolidione was not detected in both experiments, proving that the biodegradation was complete. The abiotic control experiment (i.e., without microbial inoculation) showed that no significant degradation of epindolidione was measured, indicating that the reduction in epindolidione concentration in biodegradation experiments were due to biotic causes. For the development of a biodegradation process of epindolidione at larger scale, the operating cultivation conditions were optimized in a 1.5L bioreactor using Stenotrophomonas sp. Then, we observed that the organic semiconductor steadily decreased, reaching a biodegradation of 50% during the first 10 days. This value is clearly remarkable for this type of recalcitrant compounds. For the assessment of quinacridone biodegradation, Tinto river consortium achieved a 20% removal after 20 days, but the biodegradation did not progressed at longer times. With respect to Stenotrophomonas, this bacterial strain did not show a significant capability to degrade quinacridone under these conditions. Although quinacridone is more soluble, and thus more bioavailable than epindolidione, it seems to be more recalcitrant too towards the attack of microorganisms.

The biodegradation of 2,8-difluoroepindolidione was tested with and without oxigen. Thus, under aerobic conditions, more than 70% of the initial amount of that organic semiconductor was rapidly biodegraded during the first week, reaching an approximately constant plateau were the remaining concentration of the organic compound was not affected at longer times. However, the anaerobic biodegradation process progressed more slowly, reaching a maximum biodegradation of 30% after 5-6 weeks of operation. This difference in the biodegradation extent between the aerobic and anaerobic processes is likely because the decomposition of organic compounds by bacteria preferably uses oxygen as the final electron acceptor.

9:00 AM EP03.09.04
Sustainability Assessment of Biofriendly Electronics—Establishing Best-Practice Analysis Frameworks Eric Masanet; Northwestern University, Evanston, Illinois, United States.

Sustainability assessment is an important approach for emerging technologies, as it can shed light on their potential environmental impacts and benefits when deployed at large scales, identify possible unintended consequences, and expose specific technology characteristics which can be optimized during the innovation and deployment phases to maximize future societal benefits. While there have been many life-cycle assessments (LCA) of bio-based fuels and products, applications of LCA to emerging biofriendly electronics have been much more limited. Moreover, because biofriendly electronics are a rapidly emerging class of technologies, any sustainability analysis must move beyond retrospective LCAs and be largely prospective in nature (because technological development and market data are scarce/nonexistent), requiring special care with respect to uncertainty analysis and scenario design for meaningful feedback on potential impacts and benefits. Finally, in a future requiring deep decarbonization of all economic sectors, there may be competition with prospective applications of limited global sustainable biomass resources, notably for biofuels in the transport sector, bio-feedstocks in the chemicals sector, and bioenergy with carbon capture and storage (BECCS) in the power sector; this competition may affect the sources and quality of biomass available for biofriendly electronics applications. As such the integration of LCA with dynamic energy and resource systems modeling and scenario analysis will also be necessary. Therefore, to be useful, sustainability assessment of biofriendly electronics demands a dynamic, prospective, integrated, and life-cycle systems modeling approach. This presentation will explore the development of such a best-practice assessment approach to meet this analytical vision, by reviewing strengths and weaknesses of existing modeling methods (e.g., LCA) and data sources, known data gaps and possibilities for filling them, exploring the role of lab-analysis partnerships to accelerate data availability and conduct R&D relevant scenario analyses, and propose a research roadmap for building a sustainability assessment community of practice for biofriendly electronic applications.

9:30 AM EP03.09.05

E-waste is one of the fastest growing waste streams in the world in terms of volume and its subsequent environmental impact on the planet. The global growth rate for the e-waste stream is 3–5% (Cucchiella et al., 2015) and expected to reach 50 million tonnes worldwide by the end of 2018 (Balde 2015). This e-waste stream provides an economic stream is 3–5% (Cucchiella et al., 2015) and expected to reach 50 million tonnes worldwide by the end of 2018 (Balde 2015). This e-waste stream provides an economic.
palladium but also the presence of hazardous chemicals. There are many challenges associated with the recovery of metals and non-metal fractions from e-waste due to the composite nature of these materials. The recovery of metals is the main economic driver for e-waste recycling and downstream reprocessing. The existing technologies for metal recovery from e-waste are mostly designed to capture metals. When hydrometallurgical methods are used to extract metals, fine grinding is usually required and all components are ground to very fine particle sizes. Very corrosive chemicals are commonly used to extract metals of interest, and as a result, hydrometallurgical techniques are very energy intensive and toxic residues are left after processing. Pyrometallurgical methods are also quite often used to recover metals by smelting. Both hydrometallurgical and pyrometallurgical methods are energy intensive and destructive, particularly if the focus is to only recover metals. The physical separation and step-by-step preceding final end processing allows for recovery of metals at much coarser sizes and the other non-metal materials like plastic, fiber glass, and resins to be recovered in a form that could be reused as a secondary raw material in the manufacturing of new products. This will provide an opportunity to design processes that will focus on minimizing the final residue after the recycling and end reprocessing of e-waste. The presentation will discuss current research on the step-by-step recovery of metal and non-metal fractions from e-waste.

SYMPOSIUM EP04

Soft and Stretchable Electronics—From Fundamentals to Applications
April 23 - April 26, 2019

Symposium Organizers
Roozbeh Ghaffari, Northwestern University/Epicore Biosystems Inc/MC10 Inc
Pooi See Lee, Nanyang Technical University
Marc Ramuz, MINES Saint-Étienne
Cunjiang Yu, University of Houston

Symposium Support
MilliporeSigma

* Invited Paper

SESSION EP04.01: Liquid-Material Embedded Soft Structures I
Session Chairs: Marc Ramuz and Cunjiang Yu
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 222 A

10:30 AM *EP04.01.01
Liquid Metals Encased in Functional Elastomers for Soft and Stretchable Electronics Michael Dickey; North Carolina State University, Raleigh, North Carolina, United States.

This talk will discuss recent work in our group (and through collaborations) to utilize liquid metals as electrical conductors for soft and stretchable electronics. Gallium and its alloys have low viscosity, low toxicity, and negligible volatility. Despite the large surface tension of the metal, it can be patterned into non-spherical 2D and 3D shapes due to the presence of an ultra-thin oxide skin that forms on its surface. Because it is a liquid, the metal is inherently soft and flows in response to stress to retain electrical continuity under extreme deformation. By embedding the metal into elastomer or gel substrates, it is possible to form soft, flexible, and conformal electrical components, stretchable antennas, and ultra-stretchable wires that maintain metallic conductivity up to ~800% strain. In addition to introducing the advantages of these materials for stretchable electronics, this talk will focus on recent advances with (1) patterning the metal and metal composites, (2) integrating liquid metal into functional devices including energy harvesters and transistors (in collaboration with the Ozturk and Franklin groups, respectively), and (3) encasing the metal within optimized and functional elastomers that are less prone to fail mechanically (and warn the user colorimetrically before failure, done in collaboration with the Craig group). These advances have implications for creating electronics that are softer than skin and with stretchability limited only by the encasing elastomer.

11:00 AM *EP04.01.02
Polymerized Liquid Metal Networks for Activatable Stretchable Conductors and Sensors Carl Thrasher¹, Zachary Farrell², Nicholas J. Morris¹,² and Christopher Tabor¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States; ²UES, Inc., Dayton, Ohio, United States.

Robust stretchable conductors with advanced capabilities such as stimuli-responsiveness and high power delivery over large strains are needed for advanced soft robotic, physically reconfigurable, and wearable electronic applications. Room temperature liquid metals such as eutectic gallium-indium (EGaIn) have shown potential in next generation stretchable electronic systems, but suffer from problems with containment, fabrication, and metal oxide formation. Here we synthesize phosphonic acid-functionalized reactive EGaIn core-shell particles and polymerize them on elastomer substrates to create polymerized liquid metal networks consisting of ~99.9 wt% EGaIn. Under strain the polymerized particles in the network rupture and release their encapsulated liquid metal, rapidly transitioning the network from an electrically resistive to a conductive state (10⁴ fold conductivity increase from 0-100% strain). Once activated, these network composites adopt microstructures which mitigate the deleterious effects of strain on electronic performance. As a result of these microstructures, these networks show many remarkable characteristics including increasing volumetric conductivity with strain to over 20,000 S/cm at ~700% elongation, electronic memory of previous strain states, and R/R₀ < 1 between 0-300% strain. The unique electromechanical properties of these activated liquid metal networks present a superior design strategy to provide ultra-stretchable (~300%) conductors with near-zero change in resistance and can find additional use for powerless active strain indication and triggered healing in stretchable conductors.

11:15 AM EP04.01.03
Micro-Patterned Liquid Metal Based Conductors for Large-Area Stretchable Electronics Laurent Deijace and Stephanie Lacour; Laboratory for Soft Bioelectronic Interfaces, Ecole Polytechnique Federale de Lausanne (EPFL), Geneva, Switzerland.

Gallium is a metal in a liquid state at room temperature that offers unique electromechanical properties when integrated within a soft, elastic carrier material. However, precise patterning and manipulation of the liquid metal are challenging. High surface tension prevents homogeneous spreading of liquid gallium on lyophobic silicone carriers. A thin gallium oxide skin forms immediately at the gallium surface upon exposure to ambient conditions and sets the shape of the material. We overcome these peculiar properties to pattern reliably thin gallium features with μm-scale resolution, high surface density and over centimeters side surface areas.

Our manufacturing process combines soft lithography, self-assembly and physical vapor deposition techniques, all compatible with wafer scale manufacturing. First, a PDMS layer is cast on a photoresist mold lithographically patterned with a matrix of 1.5μm thick, 5μm wide holes distributed across the entire 4in. wafer. The PDMS layer is then demolded and transferred to another carrier for further processing on the patterned side. A 160nm thick gold film is blanket-sputtered on the textured surface, so as to increase the chemical affinity of gallium to the silicone substrate. Next a tilted Ion Beam Etching (IBE) process is used to selectively remove the gold layer only above the patterned recesses. Finally,
gallium is evaporated on the substrate, where it alloys with gold and fills all empty spaces in-between the PDMS micro-posts. This process enables a range of channel designs and geometries leading to soft conductors displaying highly stable electromechanical properties when reversibly and repeatedly stretched to 50% elongation for hundred cycles. This work represents a significant advance towards the miniaturization of gallium-based technology for robust and reproducible, soft and mechanically compliant electronic circuits.

11:30 AM EP04.01.04
**Stretchable Elastic Shape Memory Fibers with Electical Conductivity**
Sungju Park¹, Hardil Shah², Neil Baugh³, Dishit Parekh³, Ishan Joshipura², Yubo Ouyang² and Michael Dickey¹; ¹Department of Polymer Nanoscience & Technology, Chonbuk National University, Jeonju, Korea (the Republic of); ²Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States.

This paper describes shape memory polymer fibers consisting of an elastic shell and a gallium liquid metal core. These fibers are interesting because they have metallic electrical and thermal conductivity, elastic mechanical properties, and excellent shape memory properties due to the ability to change the phase of the core from a low viscosity liquid to a solid metal. It is straightforward to form the fibers by via melt processing followed by injection of the liquid metal into the core. The elastic energy stored in the fiber allows it to relax back to its original geometry upon melting the solid gallium. The ability to change the core of the fiber from liquid to solid allows an enormous modulus change in the range of from 4.5 to 1618.3 MPa and the ability to have shape-memory effect; that is, the fiber can preserve a deformed shape and then return to its original shape upon heating. The shape memory behavior of these fibers is quantitatively characterized in terms of fixity (i.e. the ability to retain deformed temporal shape) and recovery (i.e. the ability to return to its original geometry). The use of a rigid metallic core provides perfect fixity. Recovery rate time is effectively minimized due to the elastomeric shell with having minimal viscous dissipation as well as rapid conversion of the metallic core to a liquid with a low viscosity. Notably, the use of gallium—with a melting point above room temperature but below body temperature—allows the user to melt and deform local regions of the fiber by hand. These stretchable elastic shape memory fibers may enable new applications in soft robotics, stretchable and wearable sensors, and bioinspired electronic skin.

11:45 AM EP04.01.05
**The Freeze/Thaw Properties of the Conformable Conductor Eutectic Gallium-Indium-Tin**
Amanda Koh¹,²; Randy Mrozek¹ and Geoffrey Slipher³; ¹U.S. Army Research Laboratory, Adelphi, Maryland, United States; ²Chemical and Biological Engineering, University of Alabama, Tuscaloosa, Alabama, United States.

Room-temperature eutectic liquid metals have become an exciting basis of research into soft materials for sensors, actuators, and robotics. This work relies on the low melting point of the liquid metal, which allows for a material which is both conformable and conductive. While the melting point of metals such as eutectic gallium-indium (EGaIn) and eutectic gallium-Indium-Tin (Galinstan) are often cited, their mechanical and electrical properties around the melting point are not well-studied. These properties, particularly the mechanical transition between a liquid and solid phase, are crucial to understanding the use of EGaIn and Galinstan as conformable conductive elements in a wide variety of environments. This work focuses on Galinstan, which is reported to have a melting point ~10°C and a low room-temperature modulus. By measuring the rheology of Galinstan between 50°C and -20°C, the range at which Galinstan can truly be called “soft” with respect to common elastomer matrices was determined. Mechanical changes caused by the effects of the freeze/thaw cycle on Galinstan were also observed. The transition between the solid and liquid state were also observed using powder x-ray diffraction to determine if a crystalline solid was formed, and what changes the freeze/thaw cycles may cause in the material. The mechanical properties of Galinstan-in-PDMS dispersions were also measured through freeze/thaw to better understand the use of Galinstan as a conformable conductor in a stretchable, electronic device. Through this work, we were able to add important mechanical performance detail to the description of Galinstan as a conformable conductor, as well as point out important considerations when manufacturing a device intended for hot and cold environments.
SELF-POWERED ULTRA-FLEXIBLE ORGANIC ELECTRONICS FOR HEALTH MONITORING

3:30 PM


FULLY IMPLANTABLE WIRELESS BATTERY-FREE OPTOELECTRONIC SYSTEMS FOR MULTIMODAL OPTOELECTRONIC NEUROMODULATION

2:45 PM

Philipp Gritsun1, Vaishnavi Krishnamurthi2, Abraham Vázquez-Guardado3, Zhaoyan Xie4, Anthony Banks5, Chun-Ju Su6, Yeshou Xu4, Chad Haney2, Emily A. Waters7, Iwährand Kandel8, Siddharth Krishnan9, Tyler Ray4, John P. Leshock9, Yonggang Huang4, Debashis Chanda2 and John A. Rogers4, University of Arizona, Tucson, Arizona, United States; 9RMIT University, Melbourne, Victoria, Australia; 3University of Central Florida, Orlando, Florida, United States; 4Northwestern University, Evanston, Illinois, United States; 2Neurolyx, Evanston, Illinois, United States.

Recently emerging classes of battery free, ultrasmall, fully implantable devices for optogenetic neuromodulation2 eliminate physical tethers associated with bulky head-stage and batteries in alternative wireless technologies and conventional setups by leveraging cellular scale light emitting diodes on flexible injectable filaments as light sources. These highly miniaturized systems enable untethered, operation for behavioral studies that eliminate motion constraints and enable new experimental paradigms in a range of complex 3D environments and contexts (e.g. social interactions) that cannot be explored with conventional technologies. These devices are, however, purely passive in their design, thereby precluding any form of active control or programmability, resulting in limitations when investigating circuit dynamics where independent operation of multiple light sources with precise active control is needed. Here we present a series of important concepts that enable controlled device operation, independent of position and angle relative to the experimental arena, with advanced wireless power harvesting capabilities and full user-programmability over multiple devices. This level of functionality is demonstrated in integrated platforms that are compatible with noninvasive imaging technologies such as computed tomography and magnetic resonance imaging and have sizes and weights not significantly larger than those of previous, passive systems. The resulting devices qualitatively expand options in brain tissue illumination for optogenetic neuromodulation and multimodal operation, with broad potential applications in neuroscience research, with specific advances in precise dissection of neural circuit function during unconstrained behavioral studies.

References

PHYSICAL BIOLOGY AND MATERIAL DYNAMICS AT THE SEMICONDUCTOR-BASED BIointerfaces

3:00 PM BREAK

3:30 PM

Self-Powered Ultra-Flexible Organic Electronics for Health Monitoring

Takao Someya1,2, Kenjiro Fukuda3 and Tomoyuki Yokota1; 1Electrical and Electronic Engineering and Information Systems, University of Tokyo, Tokyo, Japan; 2RIKEN Center for Emergent Matter Science, Saitama, Japan.

On-skin sensors have attract much attention as the next-generation wearable devices, because the conformal contact on human skin enables accurate and continuous detection of physiological signals. One of the most important technologies to improve usability of on-skin sensors is a power source to continuously supply electricity to health-monitoring systems. In this talk, we will report on recent progresses of ultraflexible organic photovoltaic cells for applications to wearable sensors. First, ultraflexible organic power sources that can be wrapped around an object have been developed with mechanical and thermal stability in long-term operation. Then, the integration of these power sources with functional electric devices including sensors has been achieved.

4:00 PM

Physical Biology and Material Dynamics at the Semiconductor-Based Biointerfaces

Bozhi Tian; The University of Chicago, Chicago, Illinois, United States.

Recent studies have demonstrated that in addition to biochemical and genetic interactions, cellular systems also respond to biophysical cues, such as electrical, thermal, and mechanical signals. However, we only have limited tools that can introduce localized physical stimuli and/or sense cellular responses with high spatiotemporal resolution. Inorganic semiconductors display a spectrum of physical properties and offer the possibility of numerous device applications. My group integrates material science with biophysics to study several semiconductor-based biointerfaces. In this talk, I will first pinpoint domains where semiconductor properties can be leveraged for biointerface studies, providing a sample of numbers in semiconductor-based biointerfaces. Next, I will present a few recent studies from our lab and highlight key biophysical mechanisms underlying the non-genetic optical modulation interfaces. In particular, I will present a biology-guided two-step design principle for establishing tight intra-, inter-, and extracellular silicon-based interfaces in which silicon and the biological targets have matched mechanical properties and efficient signal transduction. Finally, I will discuss new materials and biological targets that could catalyze future advances.

4:30 PM

Autonomic Self-Healing and Intrinsical Stretchability of PEDOT:PSS Films

Fabio Cicora; Chemical Engineering, Polytechnique Montréal, Montréal, Quebec, Canada.

Organic electronic devices, apart from consumer applications, are presently paving the path for key applications at the interface between electronics and biology. In such applications, organic polymers are very attractive candidates, due to their distinct properties of mechanical flexibility, self-healing and mixed conduction. My group investigated the processing conditions leading to high electrical conductivity, long-term stability in aqueous media as well as robust mechanical properties of the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS) [1-3]. We have demonstrated that stretchable PEDOT:PSS films can be achieved by adding a fluorosurfactant to the film processing mixture and by pre-stretching the substrate during film deposition. We have achieved patterning of organic materials on a wide range of substrates, using orthogonal lithography and pattern transfer [4-5]. Recently we have discovered that PEDOT:PSS films can be rapidly healed with water drops after being damaged with a sharp blade [6] or show autonomous self-healing if processed in presence of certain additives. My talk will deal with processing, characterization and patterning of conducting polymer films and devices for flexible, stretchable and healable electronics. I will particularly focus on the strategies to achieve films with optimized electrical conductivity and mechanical properties, on unconventional micro patterning on flexible and stretchable substrates, on the different routes to achieve films stretchability and self-healing.

References
Highly Conducting MXene Composite Fibers with Conductive Polymer Binder for Fiber-Shaped Supercapacitors

Dopamine (DA), as a crucial neurotransmitter, can transfer chemicals in human brain to affect our emotion and behaviors, and DA disorders in secretion and transportation can cause some inurable disease, such as Parkinsonism and Alzheimer's disease. Implantable flexible sensors offer a feasible approach to monitor the content and distribution of DA, and it may assist us to overcome those disease. Up to now, mainly reported investigations were conducted using electrochemical sensors modified by metallic oxide and graphene, but rough structures and limited types of above materials restrict their further development in function modulation. One of the promising strategy to meet this challenge is employing adjustable materials to combine with flexible sensors, and metal-organic frameworks (MOFs) that possess designable structures and adjustable functions can be considered as the suitable candidate for fabricating functional devices. Additionally, flexible sensors integrated with MOFs have already been achieved by our group, allowing more explorations on MOF-based flexible electronics.

Given the above consideration, this paper presents techniques and materials to fabricate a luminescent MOF-based flexible sensor, and photoelectric detector in the sensor can detect emission changes of MOF represented as functional part in response to DA. Notably, MOF-modified sensor possesses excellent biologically safety that was confirmed using live cell experiments, supplying the foundation for the practical application in living animals. This work represents the first effort in combining luminescent MOFs with flexible sensors, offering in-depth understanding of flexible sensors' property at molecular level. The excellent results may promote the progress of flexible electronics in biology, healthcare and sensing, etc.

SESSION EP04.03: Poster Session I: Soft and Stretchable Electronics—From Fundamentals to Applications
Session Chairs: Rozooheh Ghaflari, Pooi See Lee, Marc Ramuz and Cunjiang Yu
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C/E

EP04.03.01
Vapor-Phase Synthesis of Organic-Inorganic Hybrid Gate Dielectric for Flexible Electronics

Min Ju Kim1, Kwanyong Pak1, Wan Sik Hwang2, Sung Gap Im1 and Byung Jin Cho1
1Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Material Engineering, Korea Aerospace University, Goyang-si, Korea (the Republic of); 3Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Organic-based thin film transistors (OTFTs) are beneficial for wearable architecture because of their lightweight, flexibility and low cost. One of the critical issues in flexible OTFTs is gate dielectric for high performance flexible electronics. The hybrid materials consisting of organic and inorganic materials have emerged as a feasible gate dielectric for high-performance flexible electronics. Therefore, it is necessary to develop ultrathin hybrid organic-inorganic dielectrics and correlate their material properties with device performance at different bending strains. In this work, we propose a one-step synthesis method to form a high-k, ultrathin and homogeneous organic-inorganic hybrid dielectric via initiated chemical vapor deposition (iCVD). iCVD is a well-established process to deposit various functional polymer films based on a radical polymerization via a vapor-phase deposition. In this study, trimethylaluminum (TMA) and 2-hydroxyethyl methacrylate (HEMA) were used as the inorganic precursor and monomer, respectively, leading to the formation of an AlOx-embedded polymer matrix hereafter called a hybrid dielectric. The chemical bonds of the synthesized hybrid dielectric were characterized using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) which clearly demonstrated that the hybrid dielectric was successfully synthesized and deposited via iCVD process. The X-ray diffraction (XRD) spectra show that the amorphous AlOx moiety is dispersed in the polymer matrix to achieve high dielectric strength and mechanical flexibility. No apparent grain-like or pinhole-like morphologies are observed from the atomic force microscopy (AFM) images, which indicated that the hybrid dielectrics were homogeneously synthesized without any phase separation. To characterize the electrical properties of the hybrid dielectric with various Al contents, crossbar-type metal-insulator-metal (MIM) devices were fabricated. The dielectric constant was extracted from the capacitance (C) measured at a frequency (f) of 10 kHz and film thickness measured via scanning transmission electron spectroscopy (STEM). The dielectric constant (k values) increased from 3 to 7 as the Al concentration in the hybrid dielectric increased, which was attributed to a greater number of dipoles in the polymer matrix. Unlike the higher k values with higher Al concentrations, the electrical breakdown field (Ebreak) decreased linearly from 6 to 3 MV/cm, and the gate leakage current (J) at 2 MV/cm increased exponentially from 1.0 × 107 to 3.0 × 109 A/cm2. The electrical results revealed that there was a trade-off between performance and power consumption. The electrical energy bandgap (Eg) was extracted from the electron energy loss spectroscopy (EELS) with low loss spectra resulting in a wide Eg of 7.0 - 7.5 eV. Based on these preliminary experiments, the hybrid dielectric with an Al concentration of around 18% exhibited a decent k value of 6 and J value of lower than 107 A/cm2 at 2 MV/cm. The MIM device with the hybrid dielectric exhibited negligible J changes of up to 2.6 % applied strain, where the soft polymer matrix effectively released the applied strain. Finally, the iCVD hybrid dielectrics were applied to the bottom-gated OTFTs with p-type pentacene and n-type N,N′-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C13). Two typical linear and saturation operating regions emerged, revealing well-behaved transistor characteristics. The mechanical flexibility of the –p-type pentacene OTFTs with the hybrid dielectric was investigated at different bending strains. The transfer characteristics of the OTFTs were found as a function of mechanical bending strain, showing negligible changes while maintaining a low gate leakage current. The results suggest that the hybrid dielectric synthesized via the iCVD process is a promising candidate for high-performance low-power consumption flexible electronics.

EP04.03.02
Highly Conducting MXene Composite Fibers with Conductive Polymer Binder for Fiber-Shaped Supercapacitors

Jizhen Zhang, Shayan Seyedin, Zhiyu Wang, Si (Alex) Qin and Joselito M. Razal, Deakin University, Geelong, Victoria, Australia.

Fiber-shaped organic-inorganic hybrid dielectric (FSC) electrodes are beneficial for wearable architecture because of their lightweight, flexibility and low cost. Unlike the higher k values with higher Al concentrations, the electrical breakdown field (Ebreak) decreased linearly from 6 to 3 MV/cm, and the gate leakage current (J) at 2 MV/cm increased exponentially from 1.0 × 107 to 3.0 × 109 A/cm2. The electrical results revealed that there was a trade-off between performance and power consumption. The electrical energy bandgap (Eg) was extracted from the electron energy loss spectroscopy (EELS) with low loss spectra resulting in a wide Eg of 7.0 - 7.5 eV. Based on these preliminary experiments, the hybrid dielectric with an Al concentration of around 18% exhibited a decent k value of 6 and J value of lower than 107 A/cm2 at 2 MV/cm. The MIM device with the hybrid dielectric exhibited negligible J changes of up to 2.6 % applied strain, where the soft polymer matrix effectively released the applied strain. Finally, the iCVD hybrid dielectrics were applied to the bottom-gated OTFTs with p-type pentacene and n-type N,N′-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C13). Two typical linear and saturation operating regions emerged, revealing well-behaved transistor characteristics. The mechanical flexibility of the –p-type pentacene OTFTs with the hybrid dielectric was investigated at different bending strains. The transfer characteristics of the OTFTs were found as a function of mechanical bending strain, showing negligible changes while maintaining a low gate leakage current. The results suggest that the hybrid dielectric synthesized via the iCVD process is a promising candidate for high-performance low-power consumption flexible electronics.

EP04.03.03
Wearable Organic Memory Fiber for Low Voltage Operation and Conformable Data Storage


Wearable electronics have attracted attention as an emerging technology to realize practical e-textile and smart garments. For future wearable automatic systems, robust data storage media are required and process the electrical signals generated under various unpredictable strain conditions. Here, we report an organic field-effect transistor (OFET)-type memory integrated on a thin and flexible metal wire. A new fiber coating technique by using a capillary tube and controlling the solution viscosity allows the
formation of a thin and uniform organic ferroelectric film on the wire. The uniform morphology imparts excellent switching stability, long-term retention time and low-voltage operation to the flexible fiber organic memory devices. The fiber-shaped memory achieves reliable data storage even under tough environments when sewn in a stretchable textile fabric, providing the possibility of the practical, wearable fiber memory for recording electronic signals in smart textile applications.

EP04.03.04

Stretchable Location Sensor Based on Transparent AgNWs Electrodes
Hang Guo, Liming Miao, Haobing Wang, Ji Wan, Xiaoliang Cheng and Haixia Zhang; Institute of Microelectronics, Peking University, Beijing, China.

In the recent years, the smart electronic skin (E-skin) has attracted extensive attention due to the human skin provides remarkable sensor networks such as touch, temperature, vibration and pressure sensors, etc. There are many wearable electronic devices integrated with glasses and watches in the consumer electronics with the rapid development. However, all of these devices face an important issue about the stretchability which could sustain complex deformation and conformal contact with irregular surfaces. The stretchable materials are mainly required as a substrate such as organic polymer in order to make the devices stretchable. Apart from these, nanomaterials, such as carbon nanotubes, graphene and metal nanowires have been utilized to realize stretchable electronics. And the special structure designs have also played a very important role in improving stretchability. Wave, island-bridge structure, porous structure and grid structure are widely applied in these novel designs.

Herein, we developed a transparent conductive membrane which is uniform and stable even under elongation through spin-coating AgNWs solution on the stretchable substrate. The motion detection and location is indispensable for human-machine interfaces. However, as most devices work in digital method, there has been limited progress in the resolution enhancement that may lead to an increase in the number of electrodes. Therefore, the stretchable analog devices play an essential role in wearable devices, which owns higher resolution with a few electrodes. We demonstrate these new properties by using PDMS/AgNWs thin film.

A novel stretchable, transparent location sensor has been demonstrated in this work. Through the spin-coating process, the AgNWs are deposited on the surface of the PDMS substrate, which enhances the transparency and stretchability of the device. It can be attached to the human skin with conformal coverage and keep the function under the elongation of 60%. When the sensor is pressed, the position of the contact point can be acquired by the relative resistances in the analog method, which can enhance the resolution without increasing in the number of electrodes. All of the excellent properties makes the sensor have much potentials in the wearable devices and smart robots.

EP04.03.06

Soft Electronic and Optoelectronic Devices with Dynamic 3D Architectures Controlled by Heat-Responsive Polymers
Cheng Zhang and Jian Lin; The University of Missouri, Columbia, Missouri, United States.

Three-dimensional (3D) architectures qualitatively extend the functionalities of electronic and optoelectronic devices. Complex functional 3D structures have been fabricated by 3D printing, stress-controlled folding, and mechanically-guided assembly. However, the potential of 3D functional architectures built by previous methods is restrained by their static or human-intervention required dynamic structures. Herein, we demonstrate a soft 3D scaffold integrated with electronic and optoelectronic devices which can be dynamically tuned by responsive polymer substrates. The 2D films are selectively bonded onto the responsive substrates which can respond to heat simulation and actuate the assembly of the 2D films to 3D architectures. The assembled structures are dynamically controlled by the heat. The dynamic assembly is highly controllable by both experimental study and numerical simulation. Soft electronic and optoelectronic devices, i.e., a strain sensor array and a photodetector array, are integrated to the 2D films and also assembled to 3D structures. The strain sensors monitor the motion of the assembly. The photodetectors can measure both intensity and direction of incident light attributing to its 3D architecture. Moreover, the photodetector array has the capability of tracking lights incoming from all directions because its spatial configuration can be dynamically tuned by heat.

EP04.03.07

A MXene-Based Wearable Biosensor System for High-Performance In Vitro Perspiration Analysis
Yongjiu Lei; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

Wearable electrochemical biosensors for sweat analysis (e.g., glucose, lactate) present a promising means for noninvasive biomarker monitoring. However, the sweat-based measurement of the developed devices still poses many challenges: easy degradation of enzymes and biomaterials upon regular testing; the corresponding poor shelf life of the all-in-one working electrodes patterned by traditional techniques (e.g., electrodeposition, screen printing); limited detection range and sensitivity of the enzyme-based biosensors caused from oxygen deficiency in sweat. Herein, we develop a wearable multifunctional biosensor incorporating MXene/Prussian blue (Ti₃C₂Tₓ/PB) composite for durable and sensitive detection of glucose and lactate in sweat. Due to the metallic conductivity and hydrophilic nature of the MXene, greatly improved electrochemical activity was observed on the Ti₃C₂Tₓ/PB composite in comparison to previously reported Graphene/PB and CNTs/PB composites. During in-vitro perspiration monitoring, the physiochemistry signals (glucose and lactate level) could be measured simultaneously, showing high sensitivity and acceptable repeatability. A unique modular architecture design enabled a simple exchange of the specific sensing electrode to tailor to the desired analytes. Furthermore, an implemented solid-liquid-air three-phase interface design led to superior sensor performance and stability, with typical electrochemical sensitivities of 35.3 μA mM⁻¹ cm² for glucose and 11.4 μA mM⁻¹ cm² for lactate using artificial sweat. Hence, this approach represents an essential step towards the realization of ultra-sensitive enzymatic wearable biosensors for early disease identification and personalized medical applications.

EP04.03.08

Electrochemically Stable and Adherent PEDOT Coatings for High Quality EMG Recording
Niccolò Rossetti, Ada Lee, Prabhjot Kaur Luthra, Côme Bodart and Fabio Cicoira; École Polytechnique de Montréal, Montréal, Quebec, Canada.

Conductive polymers coatings on metal electrodes are an efficient solution to improve neural signal recording and stimulation due to their mixed electronic-ionic conduction and biocompatibility [1]. However, only a few studies have been reported on conductive polymers coatings on metallic wire electrodes for muscle signal recording [2]. In this work, we developed mechanically and electrochemically stable invasive electrodes for muscle signal recording in small animals based on stainless steel multi-stranded wires coated with the conductive polymer PEDOT. PEDOT doped with LiClO₄ was galvanostatically electropolymerized on stainless steel wires using three different solvents: propylene carbonate (organic), acetonitrile (organic) and water (inorganic). The coatings adhesion to the metallic substrate was tested through ultrasonication and the electrochemical stability was evaluated through phosphate buffer solution soaking test and autoclave sterilization. The solvent played a key role on the adhesion of the PEDOT coating, with organic solvents giving the best mechanical stability. Electrodes prepared with these solvents possessed excellent electrochemical stability and survived sterilization and prolonged soaking without major changes in electrochemical properties. A solution for high quality invasive muscle signal recording in small animals based on conductive polymers has been demonstrated.


EP04.03.09

3D-Printed Hydrogel with Superior Stability for Energy Harvesting and Physiological Monitoring
Min Wu, Shengjie Gao, Yixiu Wang, Ruoxing Wang and Wenzhuo Wu; Purdue University, West Lafayette, Indiana, United States.

Hydrogels have attracted much attention recently as a promising class of biomaterials. Traditional hydrogel bioelectronics are limited in several aspects, including the poor ability of the hydrogel to retain water under cold or hot environment, complicated device fabrication procedure, and complex external power requirement to drive the device. Here we propose an approach to directly fabricate hydrogel by 3D printing method, and further prepare wearable devices for self-powered sensing applications. With the addition of glycerol, the hydrogel would be able to resist a water loss and can tolerate a temperature with a wide range from -20 °C to 60 °C. The 3D printed hydrogel is able to deliver a stable triboelectric output, which can be explored as self-powered sensors for physiological monitoring. The facile 3D printing method, coupled with the water loss prevention properties
Compared to other liquids (e.g. water, ionic liquids, organic liquids), liquid metals have outstanding thermal and electrical conductivity, as well as distinct optical properties (i.e. reflectivity). As a result, they are excellent components for stretchable and soft metallic components such as antennas, electrodes, and interconnects. Thus, there is great interest in facile methods to create and pattern these liquids into useful components. The large tension and low viscosity of liquid metals presents a challenge: the metal tends to adopt a spherical shape as it exits a nozzle. There are a number of strategies to address this challenge that require the metal to directly contact other solid or visco-elastic surfaces. Here we report a way to create wires by directly extruding the metal from a nozzle. To control the shape of the liquid metal, we used electrochemical control of surface oxidation because the formation of the surface oxide significantly lowers the interfacial tension and allows the metal to adopt shapes that overcome Rayleigh-Plateau instabilities (i.e. it does not bead up). To create these wires, we pump liquid metal into electrolyte (1M NaOH). As it emerges from the nozzle, the liquid metal forms large spherical drops to minimize the surface area. However, the droplet size diminishes with an increase of potential, which indicates a decrease in interfacial tension. At a critical potential, the interfacial tension drops significantly, and the liquid metal forms wires. At larger values of electric potential (>0.8V), the oxide layer gets thicker, causing the wire to deform and turn into unusual shapes. We successfully analyze each regime of EGA as a function of flow rate and electric potential to identify conditions that form wires. The ability to deposit or remove the oxide electrochemically enables unprecedented control over interfacial activity (well beyond what is possible using electrocapillarity), which provides a means to reconfigure and manipulate the shape and position of liquid metal. This method requires minimal energy and provides reversible control of interfacial tension over an enormous range compared to conventional molecular surfactants. By adjusting the electrical potential and flow rate, the configuration of liquid metal can be manipulated on demand, which offers the possibility to create actuators or soft and stretchable analogues of rigid conductors.

Extruded Liquid Metal Wires at Room Temperature via Electrochemical Oxidation

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

Electronic skin devices capable of monitoring physiological signals and displaying feedback information through closed-loop communication between the user and electronics are being considered for next-generation wearables and the ‘Internet of Things’. Such devices need to be ultra-thin to achieve seamless and conformal contact with the human body, to accommodate strains from repeated movement and to be comfortable to wear. Recently, self-healing chemistry has driven important advances in deformable and reconfigurable electronics, particularly with self-healable electrodes as the key enablers. Unlike polymer substrates with self-healable dynamic nature, the disrupted conducting network is unable to recover its stretchability after damage. Here, we report the observation of self-reconstruction of conducting nanostructures when in contact with a dynamically crosslinked polymer network. This, combined with the self-bonding property of self-healing polymer, allowed subsequent heterogeneous multi-component device integration of interconnects, sensors and light-emitting devices into a single multi-functional system. This first autonomous self-healable and stretchable multi-component electronic skin paves the way for future robust electronics.

Fast Self-Healing and Conductive Hydrogels as Soft Strain Sensor

Yujiie Chen, Hua Li and Hezhu Liu; Shanghai Jiao Tong University, Shanghai, China.

Remarkable process achieved for conductive hydrogels has been witnessed in recent years. However, hydrogels easily damaged during the course of use, which limits their applications as soft conductors. Here, two different methods are presented to obtain multi-functional hydrogels which have fast self-healing property, conductive capability and stain-sensitive performance. In the first method, the nanocomposite hydrogel (PVA-PDA-pRGo) is designed and synthesized from polyvinyl alcohol (PVA), polydopamine (PDA) and graphene oxide (GO). Dynamic diol-borate ester bonds built from polyvinyl alcohol (PVA) and borax mainly allow nanocomposite hydrogels to display decent self-healing behaviors in mechanical (restore 92.89% of original tensile strength within 60s), electrical (restore 96.7 ± 2% of original resistance within 4.2s) and rheological recovery experiments without any external stimuli. Graphene oxide (GO) is partially reduced under the oxidative self-polymerization of dopamine (DA), providing conductivity for nanocomposite hydrogels (2.7 mS cm⁻¹). In the second method, physically crosslinked oxidized sodium alginate (OSA)/poly(acrylic acid) hydrogel (OSA/PAA-Fe3+) are synthesized by one-pot free radical polymerization. Both hydroxyl and carboxyl groups on oxidized sodium alginate chains were involved in coordination with Fe3+, which endowed the hydrogel with double network structure. OSA/PAA-Fe3+ hydrogels have excellent mechanical properties, like tensile strength up to 0.1MPa and elongation up to 1500%. The self-healing experiment showed that the self-healing efficiency of OSA/PAA-Fe3+ hydrogels can reach about 90% within 4 hours at room temperature. Furthermore, all of the hydrogels prepared by these two ways demonstrate strain sensitivity in the designed LED bulb circuit. In view of no apparent anaphylaxis of nanocomposite hydrogels in human skins, the soft stain sensor prepared by designed hydrogel can be fabricated to detect human activities, such as bending and sitting. Our work offers an effective approach to synthesize a fast self-healing, conductive and strain-sensitive hydrogel applied as soft strain sensor for human movement monitoring.

Planting Carbon Nanotubes onto Supramolecular Polymer Matrixes for Waterproof Non-Contact Self-Healing

Bo Li and Ning Ma; College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, China.

Supramolecular polymers show unique and excellent properties due to the reversible and designable nature of the non-covalent interactions. Herein, ureido-pyrimidionone (UPy)-based supramolecular polymers were employed to fabricate the thermo-responsive composite materials with multi-walled carbon nanotubes (MWCNTs) by planting the MWCNTs onto the supramolecular polymer matrix via a simple surface spraying procedure. The MWCNTs coating on the surface of the supramolecular polymer matrix gave the composite film superhydrophobic and conductive properties, and it had a non-contact healable ability under water 808 nm near-infrared light (NIR) irradiation. Moreover, the UPy-based supramolecular polymer acted as thermo-responsive matrices to guarantee the self-healing properties at a relatively low temperature, such as body temperature (33 °C–34 °C). The supramolecular polymer/ MWCNTs composite materials exhibited excellent strain sensitivities and could be used to prepare human motion-monitoring devices. Meanwhile, non-contact IR or body temperature self-healing property will greatly extend the life of the device. It provides a promising possibility for the development of the next generation of health monitoring system applied in underwater environments. This line of research may find a promising practical application in healable wearable devices used in particular conditions. And we hope this scheme can provide a new avenue for the design and preparation of functional devices with supramolecular polymeric materials. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

Pressure-Sensitive Rectifier Array for High Resolution E-Skin Tactile Sensor

Insang You, Minsik Kong and Unyong Jeong; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

E-skin tactile sensors mimicking human mechanoreceptors have been studied intensively and expected to be applied to various future electronics such as haptic device, robot tactile sensor, human-machine interface, prosthetic appliances and implantable electronic devices. To imitate the human cutaneous tactile sensors, E-skin is characterized by extreme mechanical flexibility or deformability and excellent recognition of force distribution. The mechanical flexibility of the E-skin has been successfully achieved using ultrathin substrates or stretchable interconnection between the rigid sensor units. Those device structures minimize the stress accumulated on the device units so that E-skin can operate under repeated stretches. The breakthroughs open the possibility of fabricating printed active matrix tactile sensors. In order for E-skin to sense the spatial distribution of mechanical stimulation, a large number of sensors must be integrated to provide enough spatial resolution. For this purpose, some advances have been made in the fabrications of transistor-operated tactile sensor arrays. Although the transistors could prevent electrical crosstalks between the pixels and greatly reduce the complexity of the transistor-based device is high. Active matrix structure is advantageous for individual pixel operation especially for highly integrated devices such as display or memory. However, in terms of E-skin tactile sensors, a passive device with a simple two-terminal structure would be more desirable to achieve high flexibility or deformability simultaneously with enough spatial resolution. Using a rectifying diode can be another approach to remove the electrical crosstalks. Someya and coworkers fabricated a pressure sensor matrix in which each cell was composed of a resistor-selector combination. They developed a mechanically robust organic diode and integrated a pressure sensitive elastomer resistor on top of the diode layer, which was the first demonstration using the rectifying diode for a flexible tactile sensor. This type of
In neuroscience, weakly electric fish are used to study how motor signals influence sensory processing [1-3]. Specifically, understanding how information is encoded in the precise timing of electrotactile spikes relative to sensory inputs will significantly contribute to behavioral studies. Previously, stimulating the electrotactile receptors of weakly electric mormyrid fish has been restricted to dipole current sources [4]. In this work, we present a dense flexible electrode array that conforms to the fish’s skin and is seamlessly integrated with a robust user interface. The electrode array consists of 96 square electrodes with a side length of 250 μm and diagonal spacing of 1 mm. The pattern was chosen to match the hexagonal pattern of the fish’s electrosensors. Gold electrodes were photolithographically patterned on parylene-covered spin-coated PDMS, as shown in multiple previous studies [5,6]. A second parylene layer was deposited and patterned to encapsulate the electrode traces and avoid crosstalk between electrodes. Chemical surface modification was completed to match the surface energy of the fish’s skin for several days. A multiplexer based circuit was used to individually select electrodes. A LabVIEW program allows a user to choose an electrode and synchronize the electrode’s information with neurophysiological data acquisition software. Local field potential was measured in the electrosensory lobe of the hindbrain while individually driving electrodes. Results demonstrate that this system is satisfactory for more complex neuroscience experiments.


Neuromorphic electronics is promising to process complex real-world problems such as visual information, speech recognition, and body movement control based on their compactness, fault tolerance, and high-energy efficiency. Artificial synapses are rapidly emerging for neuromorphic electronic devices that emulate biological nervous systems. Emulating learning and memory functions of the brain is the main focus in neuromorphic electronics, but mimicking the complicated biological sensory and motor nervous systems that operate sequential functions related to proprioception, signal processing, and a motor response is also a challenging issue especially to realize bio-inspired soft robotics and electronics. Herein, we demonstrate flexible and stretchable organic artificial synapses for sensory and motor nervous systems of bio-inspired electronics. Sensory and motor electronic nerves are demonstrated by integrating organic synapses with sensory and motor organs. The sensory organs detect stimuli and fire artificial neural signals which will be transmitted to organic synapses as presynaptic action potentials. The flexible and stretchable organic synapses which are favorable for soft robots generate a post-synaptic response which will stimulate motor neurons and muscles. Thus, we realize i) a hybrid reflex arc system composed of artificial pressure-sensory nerves and biological motor nerves in a detached insect leg, and ii) artificial sensorimotor nervous system composed of an artificial light-sensory receptor and electronic neuromuscular system with an artificial muscle fiber. In addition, we demonstrate that these neuromorphic systems are promising to develop human/machine interface by distinguishing braille characters and conducting wireless optical communication. We can reasonably derive that this system is satisfactory for more complex neuroscience experiments.
The adoption of a thin-film substrate is a key aspect for the development of skin-contact imperceptible devices, in the so-called cutaneous or epidermal electronics. Together with reducing the thickness, lowering the mismatch in the mechanical properties of the device, with respect to the skin’s own, plays a major role. These properties reflect in devices inherent bending stiffness, determining their ability to flex to small curvature radius, following the skin relief profile in conformal adhesion. Temporary Tattoo Electrodes (TTEs) were developed to meet these requirements. TTEs are all made by polymers and their overall thickness is < 1-2 μm. They are fabricated by inkjet printing of the conductive polymer PEDOT:PSS on top of commercially available temporary tattoo paper. Recently, ultraconformable TTEs have been adopted in the recording of many electrophysiological signals and compared with standard Ag/AgCl electrodes. Wet Ag/AgCl electrodes are routinely used in electrophysiology (EP) thanks to their high signal quality. On the other hand, these electrodes exhibited many disadvantages which impose severe restrictions in all EP applications. The major issues are related to their limited time stability, due to gel drying, and to their cumbersome nature. With TTEs we showed the recording of electrocardiography (ECG) and electromyography (EMG) demonstrating their outstanding capabilities in interfacing with human body (1,2).

Now, we investigated the recording of electroencephalography (EEG) signals, the most challenging scenario due to the weakest signal and the lowest frequency range in EP (typical 10 - 100μV signal amplitude, frequency components 0.5Hz - 100Hz), EEG monitoring was performed in a clinical environment with the aim to open for new perspectives in EEG. TTEs have been thus tested in different clinical conditions, to cover the most of EEG diagnostics. We firstly validated TTE with the recording of alpha waves, the most known and studied brain rhythm. TTEs were also compared with Ag/AgCl electrodes, through Power Spectral Density (PSD) assessment, showing a good match over the whole signal spectrum. TTEs were further evaluated in auditory evoked potentials (AEP) measurements, in comparison with the standard Ag/AgCl electrodes, exhibiting comparable at all results. Furthermore TTEs’ compatibility with magnetoencephalography (MEG) equipment have been performed. EEG/MEG are frequently used in combination and at the best of our knowledge this is the first time that a dry electrode exhibits complete compatibility with MEG. The successful evaluations of TTEs in the EEG field paves the way for future development of imperceptible alternatives to standard electrodes in clinical practice.


10:00 AM BREAK

SESSION EP04.05.01

Hydrogels Sense and Heal Better with MXene Yizhou Zhang, Kanghyuck Lee and Husam N. Alsharief; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Conductive hydrogel-based strain sensors hold great promise for wearable electronics, point-of-use medical sensors, and soft robotics. However, their sensitivities are generally low and they suffer from signal hysteresis and fluctuation due to the viscoelastic property, which can compromise their sensing performance. In our recent work, we prepared MXene (Ti3C2Tx-based Poly (vinyl alcohol) (PVA) hydrogel (M-hydrogel) via a simple method [1]. The obtained M-hydrogel sensor exhibits high strain sensitivity with remarkable stretchability, instantaneous self-healing ability, excellent conformability, and adhesive prowess to various surfaces including the human skin.

More importantly, the M-hydrogel shows much higher sensitivity under compressive strains than tensile strains. This asymmetrical strain sensitivity coupled with viscous deformation (self-recoverable residual deformation) is for the first time proposed to add new dimensions to the sensing capability of hydrogels: both direction and speed of motions on the hydrogel surface can be detected conveniently. Based on this effect, the M-hydrogel shows superior sensing performance in advanced sensing applications such as recognition of signature and vocal signals. Thus the traditionally disadvantageous viscoelastic property of hydrogels is turned into an advantage for sensing, which reveals new prospects for hydrogel sensors.


10:45 AM EP04.05.02

Bioimpedance Spectroscopy with Conformal Polymer Electrodes and Its Application in Long-Term Health Monitoring Jae Joon Kim, Linden Allison and Trisha L. Andrew; Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Conformal polymer electrodes can be vapor printed directly onto the surfaces of living organisms without damaging their health and self-sustenance. These polymer electrodes can then be used as contact pads for bioimpedance spectroscopy, which reveals detailed information about the health of the organism. Notably, polymer electrodes can be created directly on living plants, meaning that bioimpedance measurements can be performed on-demand, throughout the growth cycle of a plant. Vapor-printed polymer electrodes, unlike their adhesive thin-film counterparts, do not delaminate from microtextured living surfaces as the organism matures and do not observably attenuate the natural growth pattern and self-sustenance of the plants investigated herein. Deep tissue damage caused by dehydration and UVA exposure can be reliably detected throughout the life cycle of a plant. Long-term plant health monitoring will find strategic use in food farming, crop management, and biohazard signaling.

11:00 AM EP04.05.03

3D Designed Ion Selective Sensors Chao Bao and Woo Soo Kim; School of Mechatronic Systems Engineering, Simon Fraser University, Surrey, British Columbia, Canada.

Requirement of real-time health monitoring boosts the development of wearable electronics. Especially cutting-edge technologies of integrated circuit board have been successfully utilized to obtain flexible devices. Here we report development of 3D ion selective field sensors integrated by 3D printing as ion selective field effect transistors (ISFETs). Separately fabricated FETs and ion selective membranes are both verified before hybridization. Then, the combined ISFETs show high sensitivity to ammonium (NH4+), potassium (K+), and calcium (Ca2+) ions with linear responses depending on ion concentrations. Moreover, high selectivity of these ISFETs has also been proved during the interference tests, not only by the separate interference ions testing, but also by artificial saliva with multiple interference ion concentrations. Additionally, unique wireless protocols for the 3D printed ISFET has also been implemented. The AC output signal converted from DC input during this signal transmission process is identified as the ion concentration. This new wireless sensing protocols open the potential of the 3D printed ISFETs in the field of wireless health monitoring sensors.

11:15 AM *EP04.05.04

Stretchable Conductive Nanocomposite for Implantable and Wearable Bioelectronics Dae-Hyeong Kim1, 2; 1Seoul National University, Seoul, Korea (the Republic of); 2Institute for Basic Science, Seoul, Korea (the Republic of).

Intrinsically stretchable conductors form a vital component of advanced soft bioelectronics. And novel nanocomposites based on conductive nanomaterials have been used in diverse applications of implantable and wearable bioelectronics. Among many nanomaterials for the composites, silver nanowires (Ag NWs) have been popular. However, achieving highly conductive and soft composite simultaneously is challenging. Furthermore, because bioelectronics is necessarily exposed to biofluids, preventing Ag NW oxidation and Ag ion leaching is a significant challenge. Here we have achieved a highly conductive, biocompatible, and soft nanocomposite by using silver chloride (Ag-Au) core-sheath NWs and polystyrene-butadiene-styrene (SBS) elastomer. We synthesized ultralong Ag NWs encapsulated with a smooth and uniform Au sheath and then mixed them with the polymer. Phase separation of Ag-Au NWs and SBS occurs, which forms microstructures in the composite, reduces Young’s modulus, and increase softness and conductivity of the composite. We used the nanocomposite to fabricate a customized multi-channel soft cardiac mesh for the diseased swine heart. The mesh could be also fabricated as a wearable device which monitored electrophysiological signals and applied electrical and thermal stimulations on the human skin.

*EP04.05.04

Stretchable Conductive Nanocomposite for Implantable and Wearable Bioelectronics Dae-Hyeong Kim1, 2; 1Seoul National University, Seoul, Korea (the Republic of); 2Institute for Basic Science, Seoul, Korea (the Republic of).

Intrinsically stretchable conductors form a vital component of advanced soft bioelectronics. And novel nanocomposites based on conductive nanomaterials have been used in diverse applications of implantable and wearable bioelectronics. Among many nanomaterials for the composites, silver nanowires (Ag NWs) have been popular. However, achieving highly conductive and soft composite simultaneously is challenging. Furthermore, because bioelectronics is necessarily exposed to biofluids, preventing Ag NW oxidation and Ag ion leaching is a significant challenge. Here we have achieved a highly conductive, biocompatible, and soft nanocomposite by using silver chloride (Ag-Au) core-sheath NWs and polystyrene-butadiene-styrene (SBS) elastomer. We synthesized ultralong Ag NWs encapsulated with a smooth and uniform Au sheath and then mixed them with the polymer. Phase separation of Ag-Au NWs and SBS occurs, which forms microstructures in the composite, reduces Young’s modulus, and increase softness and conductivity of the composite. We used the nanocomposite to fabricate a customized multi-channel soft cardiac mesh for the diseased swine heart. The mesh could be also fabricated as a wearable device which monitored electrophysiological signals and applied electrical and thermal stimulations on the human skin.
11:45 AM EP04.05.05
Ionic Liquid Doping Enables High Transconductance and High Ion Sensitivity in Flexible, Stretchable Organic Electrochemical Transistors Xihu Wu, Abhijith Surendran, Jieun Ko and Wet Lin Leong; Nanyang Technological University, Singapore, Singapore.

Organic electrochemical transistors (OECTs) are highly attractive for applications ranging from circuit elements, neuromorphic devices to transducers for biological sensing and the archetypal channel material is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS. The operation of OECTs involves the doping and de-doping of a conjugated polymer due to ion intercalation under the application of a gate voltage. However, the challenge is the trade-off in morphology for mixed conduction since good electronic charge transport requires a high degree of ordering among PEDOT chains, while efficient ion uptake and volumetric doping necessitates open and loose packing of the polymer chains. Here we demonstrate ionic liquid doped PEDOT:PSS that overcomes this limitation. Ionic liquid doped OECTs show high transconductance, fast transient response and high device stability over 3600 switching cycles.[1] The OECTs are further capable of having good ion-sensitivity and robust towards physical deformation. These findings pave the way for higher performance bioelectronics and flexible/wearable electronics.


SESSION EP04.06: Liquid-Material Embedded Soft Structures II
Session Chairs: Roosbeh Ghafarli and Cunjiang Yu
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 222 A

1:30 PM EP04.06.01
From Particles to Parts—Multi-Phase Metallic Particle Additives for Sensing and Tunable Materials Rebecca Kramer-Bottiglio; Yale University, New Haven, Connecticut, United States.

Particles made from liquid or low-melting-point alloys can be leveraged to create a new class of functional responsive composite materials. In this talk, I will present two types of metallic particles: eutectic gallium-indium particles and Field’s metal particles. Eutectic gallium-indium particles have been used to achieve printable, soft, and stretchable electronics. More recently, we have demonstrated the role of Field’s metal particles in enhancing the range of stiffness properties in a thermally responsive epoxy, and in creating variable elasticity and switchable anisotropy when embedded in silicone elastomer. These responsive material properties derived from metallic particle additives enable new capabilities for wearables, soft electronics, and soft robotics.

2:00 PM EP04.06.02
Electrical Control of Shape in Liquid Crystalline Elastomer Nanocomposites Tyler Guin1,2, Timothy White1 and Amit Naskar2; 1Air Force Research Laboratory, Wright Patterson AFB, Ohio, United States; 2Physical Sciences Directorate, Oak Ridge National Lab, Oak Ridge, Tennessee, United States; 3University of Colorado Boulder, Boulder, Colorado, United States.

Liquid crystal elastomers (LCEs) are soft, anisotropic materials that exhibit large, reversible shape changes in response to external stimuli. The director (average alignment) of an LCE can be localized into pixels via photoalignment. By rationally designing the director profile, out-of-plane shape transformations are possible when the material is activated. In this talk, single-wall carbon nanotube – LCE nanocomposites are presented, and their distinctive electromechanical actuation explored. When a DC electric field is applied through the material thickness, the composite waxes and wanes along the alignment direction. By localizing the orientation of the LCE and SWNT via photoalignment, complex 3-D shapes can be electrically triggered. Additionally, a brief explanation of the novel electrostrictive mechanism will be presented.

2:15 PM EP04.06.03
Mechanical Tunability of Core-Shell Liquid Metal Nanoparticles for Self-Healing Electronics Nicholas J. Morris1,2, Zachary J. Farrell1,2, Carl Thrasher1 and Christopher Tabor1; 1RXAS, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States; 2URE, Inc., Dayton, Ohio, United States.

A vision for many potential applications of flexible and stretchable electronics has led to new and diverse research approaches in the previous decade, such as intrinsically stretchable organic electronics and strain relief geometries in otherwise non-compliant traditional materials. A third approach is to engineer materials to respond and adapt to strain by repairing themselves through self-healing mechanisms. In this work, we utilize the stimulus-responsive characteristics of a colloidal room temperature eutectic gallium-indium alloy (EGaIn) to achieve electronic self-healing triggered by strain and mechanical damage. Unlike organic conjugated systems, EGaIn possesses the high conductivity of a metal and while its fluidic properties allow it to flow and adapt to induced strain. We utilize EGaIn’s intrinsic ability to grow a native passivating viscoelastic oxide skin to produce liquid metal core-shell nanoparticles, serving as small reservoirs of the fluidic metal core, which upon rupture provide the potential to reconnect damaged electronic components and restore electrical connectivity. We report on our ability to modify the mechanical properties of the core-shell nanoparticles by correlating changes in stiffness, shell modulus, and ultimately the rupture force required to induce healing with various chemical treatments of the oxide shell (Farrell et al., Langmuir 2018). Flat-punch nanoindentation techniques with in situ electrical characterization were developed to experimentally characterize single particle stiffnesses and the critical buckling loads associated with particle rupture which would lead to electrical restoration. The modulus of the oxide shell was estimated using Reissner’s elastic thin plate theory, with estimated moduli between 0.37-1.38 GPa depending on functionalization. A fifty-fold increase in critical buckling load was measured across the various particle systems, providing a large range of engineering control and allowing application specific mechanical properties for implementation in self-healing coatings, stretchable conductors, and push-to-connect low temperature solders. In light of the standalone nature of the particle system, we anticipate their addition to existing electronics in a variety of ways, such as chemical binding through ligand anchoring, spray coating, or drop casting; imparting healing functionality and mechanical robustness to traditional electronic materials.

2:30 PM BREAK

SESSION EP04.07: Robotics, Prosthetics and Eskin I
Session Chairs: Roosbeh Ghafarli and Cunjiang Yu
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 222 A

3:30 PM EP04.07.01
Emerging Self-Healing Material and System Platforms for Electronic Skins in Wearables and Robotics Benjamin C. Teso1,2,3; 1Materials Science and Engineering, National University of Singapore, Singapore, Singapore; 2Institute of Materials Research and Engineering, Singapore, Singapore; 3Biomedical Institute for Global Health Research and Technology, Singapore, Singapore.

The multi-disciplinary efforts in the last few decades have enabled mechanically softer and skin-like electronic devices1–5. These exciting progress opens multiple doors of opportunity to utilize innovative materials and devices intimately with epidermal surfaces, wearable technologies and robotics. In this talk, I will discuss some of the new material platforms we are developing for more robust human-machine interactions, such as self-healing stretchable optoelectronics devices. At the same time, I will also present our efforts
in developing new system architectures to scale the density and number of such devices for rapid environment perception. Such system architectures can be broadly applied in electronic skins, and has broad potential for continued applications in wearables, brain-machine interfaces, prosthetics and robotics.

References

4:00 PM EP04.07.02 Stretchable, Transparent and Breathable Epidermal Electrode for Health-Related Applications You Jun Fan, Lu Liu, Xin Li and Guang Zhu; Beijing Institute of Nanoenergy and Nanosystems, CAS, Beijing, China.

Recently emerged electronic skins with applications in on-body sensing and human–machine interfaces call for the development of high-performance skin-like electrodes. In this presentation, a family of recently developed stretchable, transparent, and breathable epidermal electrode will be introduced, which is composed of a nanofoils scaffold and a silver nanowires network.

Through techniques such as vacuum filtration or electro-spinning/electro-spraying, the silver nanowires are embedded into a scaffold made of polymer nanofibers. Optical transmittance of 84.9% at 550 nm wavelength is achieved at a significantly low sheet resistance of 8.2 Ωsq⁻¹. The resistance of the epidermal electrode only slightly increases by less than 0.1% after being bent for 3000 cycles at the maximum curvature of 300 m⁻¹ and by less than 1.5% after being dipped in saline solution for 2500 cycles. Attributed to silver nanowires with hierarchical dimensions, great robustness against tensile strain is achieved. The reinforcement from the nanofoil-based scaffold as a backbone maintains the connections among the Ag nanowires by undertaking most of the loaded stress. The epidermal can still maintain its conductivity when experience a strain of over 300%.

The epidermal electrode can form tight and conformal bonding skin through Van Dal Walls force. Because of the conformal contact as well as the high conductivity, the epidermal electrode shows a contact impedance 50% lower than commercial gel-based electrode. As a result, the epidermal electrode exhibits apparently higher noise resistance again body motions when measuring physiological signals such as ECG, making it promising to be used in ambulatory on-body monitoring for healthcare applications. Besides, the epidermal electrode allows the evaporation of perspiration, making it suitable for long-time use.

4:15 PM EP04.07.03 Fully Wirelessly-Operated Soft Actuators with Environmental-Sensing Capability Byungkook Oh, Young-Geun Park, Sangyoon Ji, Woon Hyung Cheong and Jing-Ling Park; Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of). The most important function in soft robotics is to travel through harsh spaces and receive the real-time sensing signals wirelessly based on today’s smart technologies. However, to date, the reported soft robotics has the limitation of low degrees of freedom of movement because tethered systems should be connected to soft actuators to initiate the actuation. Although few research groups have demonstrated an untethered soft actuator, the reported untethered soft actuators only mimicked the movement of people or animals without any environmental-sensing capability. The key requirements for designing human-like soft robots with somatosensory systems are to operate the soft actuators without supporting equipment and to have wireless environmental-sensing capability. Fabricating fully wirelessly-operated soft actuators with environmental-sensing capability has advantages of improving degrees of freedom of movement and adapting them to various applications like biomedical fields. For the Internet of Things (IoT)-based smart wireless environment, providing wireless environmental-sensing systems has highlighted the need for using the electronic sensors and integrating them to a soft actuator body. However, the conventional electronic sensors are rigid, the integration of the electronic sensors to the soft actuator body has challenges for poor adhesion between electronic circuits and the soft actuator body and low reliability and stability of electronic sensors due to their rigid properties. Thus, improving the reliability of electronic sensors is essential for the advances in soft robotic fields. Herein, we report an unconventional approach for demonstrating fully wireless soft robotics with wireless tactile-sensing systems. The electrothermally-activated phase transition soft actuator is composed of the entirely soft and flexible body matrix so that the rate of initiating the actuation of the soft actuators increases. Soft actuators we designed are integrated to a pressure sensor and temperature sensor with improved stability and reliability due to conformal actuating properties, causing the actuation strain to distribute throughout the entire soft body actuated. However, it still has a problem of generating of electron-hole pairs (EHPs) in pressure sensors as the temperature of flexible heaters increases. The generation of EHPs results in the increase in the output current. Thermally excited charge carriers can affect the sensing signals of pressure sensors. Evading the generation of EHPs is an important feature for the sensory system to receive pressure sensing information exclusively. To that end, we designed the configuration of pressure sensor and temperature sensor above the heater film. By integrating them in parallel above the soft body frame, only tactile sensing signals can be received with calibration steps using sensing signals of the temperature sensor. It provides the pressure sensors are independent of the increasing temperature of heaters. Our soft actuators can be actuated wirelessly with remote temperature control systems interconnected to heaters. And, they can also receive real-time sensing feedback wirelessly by connecting the wireless pressure sensory module to electronic sensors. Our demonstration of wireless actuation of soft actuators with wireless environmental-sensing capability suggested that the soft actuator has an important feature for providing the capability of the use in the harsh spaces.

4:30 PM EP04.07.04 Liquid Crystal Elastomers for Soft and Stretchable Bioelectronics Jinn Maeng, Hyun Kim, Mahajbeen Javed and Taylor Ware; Bioengineering, The University of Texas at Dallas, Richardson, Texas, United States.

Achieving implantable devices that reside in human body with chronic stability has long been a goal of the bioelectronics community. A major challenge in achieving long-term stability lies in the difficulty in establishing reliable interconnection of the implantable devices to the outside world. For example, implantable neural devices in the periphery undergo significant strain due to repeated muscle flexion and extension. Furthermore, device encapsulation can be significantly weakened under such strain, causing infiltration of physiological fluids into devices that leads to chronic failure. Therefore, efforts toward developing implantable electronics based on high barrier and strain tolerant materials are needed.

Here, we present a liquid crystal elastomer (LCE)-based, soft, and stretchable electronics architecture for their potential as a platform for chronic implantable bioelectronics. The unique shape-morphing capability of LCE is leveraged to fabricate electronic devices in strain tolerant three-dimensional (3D) shapes. Specifically, we employ LCEs as substrates for electronic devices that are flat during processing but then morph to 3D shapes for use. A variety of thin-film electronic components, including conducting traces and metal-insulator-metal (MIM) capacitors, is fabricated on surface-aligned LCE substrates by using photolithographic microfabrication processes. These devices are shown to morph their shapes from 2D to 3D as programmed, upon the release of the LCE films from the carrier wafer. The 3D helical cable conductors and capacitors created by this method demonstrate strain tolerance up to 100% with less than a 5% change in resistance or capacitance. We will discuss the mechanical and electrical properties of these cables with various encapsulation coatings including parylene-C, AlOx/parylene-C bilayer, and LCE. Our preliminary results suggest that the LCE-based soft electronics technology proposed herein may open up a new avenue for developing chronic implantable bioelectronics and neural interfaces.

4:45 PM EP04.07.05 3D Printing Flexible Silicones, TPUs and Nylon Materials for Actuating Devices and Motors Rigoberto C. Advincula; Case Western Reserve University, Cleveland, Ohio, United States.

The application of silicones and thermoplastic polyurethanes (TPUs) in the number of electronic and flexible device applications has multiplied through the years with its excellent composition control and the ability to prepare various forms primarily through the injection molded and thermo-formed processing shapes. This means that their thermo-mechanical properties can be tuned towards more mechanically compatible properties to the human body including elastomeric properties. However, in a number of prosthetics devices including artificial body parts, sensors, implants, etc. 3D printing is emerging to be an alternative for additive manufacturing with its rapid-prototyping advantage and the ability to incorporated new polymer and nanocomposite in processing methods such as fused deposition modeling (FDM), stereolithographic apparatus (SLA) and viscous solution printing (VSP). It should be a viable method for the limited and specific production of flexible electronic devices that are fit even for personalized healthcare. This talk will highlight our work on 3D Printed Silicones, 3D printed TPU, etc. and 3D Printed nylons, to form basic material compositions flexible <span style="background-color:rgb(246, 213, 217);"—electronic nanocomposite materials containing graphene, carbon nanotubes, carbon black), etc. </span> Structure-property relationships correlated with the formation
of improved modulus and flexural strength with increasing amounts of electronic nanofiller components.

SESSION EP04.08: Poster Session II: Soft and Stretchable Electronics—From Fundamentals to Applications
Session Chairs: Roozbeh Ghaffari, Pooi See Lee, Marc Ramuz and Cunjiang Yu
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

EP04.08.01
NIR Absorbing Ionic Dyes for Transparent Photo-Actuators Minsu Han, Lim Hanwhuy, Jongun Hwang and Eunyongu Kim; Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea (the Republic of).

Photothermal materials absorbing near infrared light have received strong attention for optical filters, sensors, energy harvesters, and photothermal theragnosis agents. In particular, NIR absorbing ionic dyes containing multi aromatic units have high transparency and optical selectivity, so that they are challenging materials as a transparent photothermal material. However, the researches on these materials are rather limited due to the multi-step synthetic process as well as difficulty in the characterization of molecules. Herein, we report synthesis and application potential of NIR absorbing ionic dyes as a photo-actuating electrode. NIR absorbing ionic dyes were synthesized through modification of aromatic amines over >80% yields, and characterized by spectroscopic methods. The ionic dyes showed strong absorption of NIR light at ~ 1000 nm region, while they were transparent in visible region (%T > 90) both in solution and film state (Fig. 1(a)). Thin film of the ionic dyes was applied to a photothermal actuator, which showed large temperature rise upon exposure to a NIR light (Fig. 1(b)). The temperature rise, transparency, and photo-actuation of the transparent actuator of the ionic dyes will be presented.

EP04.08.02
Thermally Self-Healing Electrochromic Film and Devices Derived from Reversible Diels–Alder Polymer Yi Wang and Chunyang Jia; School of Electronic Science and Engineering, Chengdu University, Chengdu, China.

The cracking of electrochromic materials due to aging or reiterative bending is a major problem which noticeably degrades the performances of electrochromic devices. In this research, a novel self-healing electrochromic polymer PPFMA was synthesized, which integrated the electrochromic triphenylamine and self-healing Diels-Alder groups. The PPFMA film showed all superior electrochromic properties, such as stable color changes (yellow to green to blue) with a maximum optical contrast of 42.7% at 1050 nm and high coloration efficiency of 108.3 cm2/mC. Meanwhile, the polymer PPFMA also showed excellent self-healing performance, cracks cut on the film surfaces (bleached or colored states) could be self-healed at 110 °C within 4 min, and the self-healing rate was about 80%. The results indicate that the polymer PPFMA has the mutual independent bifunction of electrochromic and self-healing, it is a promising material for prolonging the service life of electrochromic device.

EP04.08.03
Highly Robust, Transparent and Breathable Epidermal Electrode Yousun Fan; Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China.

Recently emerged electronic skins with applications in on-body sensing and human-machine interface call for the development of high-performance skin-like electrodes. In this work, we report a highly robust, transparent, and breathable epidermal electrode composed of a scaffold-reinforced conductive nano-network (SRCN). Solution-dispersed silver nanowires, through facile vacuum filtration, are embedded into a scaffold made of polyanime nanofibers. Optical transmittance of 84.9% at 550 nm wavelength is achieved at a significantly low sheet resistance of 8.2 Ω sq−1. The resistance of the SRCN only slightly increases by less than 0.1% after being bent for 3,000 cycles at the maximum curvature of 300 m−1 and by less than 1.5% after being dipped in saline solution for 2,500 cycles. The excellent robustness is attributed to the reinforcement from the nanofibers-based scaffold as a backbone that maintains the connections among the silver nanowires by undertaking most of the loaded stress. The SRCN not only forms tight and conformal bonding with target surface but also allows the evaporation of perspiration, making it suitable as an epidermal electrode for long-time use. Furthermore, fine and clean-cut circuit patterns with line width on the micrometer scale can be readily prepared, paving the basis for fabricating sophisticated functional electronic skins.

EP04.08.04
Patterned Transfer of Silver Nanowire Electrode by Using UV Curable Pressure Sensitive Adhesives KeumHwan Park1, Ye-seul Song1, Hee-Jin Lee1, Woongsik Jang2, Dong Hwan Wang2 and Youngmin Kim1; 1KETI, Sungnam-si, Korea (the Republic of); 2Chung-Ang University, Seoul, Korea (the Republic of).

Recently, studies on the fabrication of stretchable electrodes using AgNW have attracted much attention. Among the many methods, stamping transfer process is most considered as an advanced technology which can overcome the limitations of existing methods such as lithography, and wet coating. In this study, UV curable pressure sensitive adhesives (PSAs) consisting of acrylic adhesives and UV curable oligomers are prepared. The novel UV curable oligomers are synthesized through two steps. The anilinolysis of the cyclic carbonate with amine-capped polypropylene glycols (PPGs) afforded multifunctional alcohols in the first step. Next, the reaction between the alcohols and methacryloyl isocyanates produced multi-arm PPG methacrylates. These compounds were mixed with the acrylic adhesive to generate two kinds of UV curable PSAs. The peel strength of the two PSAs on th PC substrate was 1,113 g/in, and 991 g/in, respectively. Interestingly, the peel strength of the PSAs was reduced by two orders of magnitude after UV irradiation. The initial tack forces of the PSAs also were dramatically reduced. The reduced adhesion of the PSAs was attributed to the high storage moduli induced by UV treatment. The UV curing of PSAs was confirmed by monitoring the disappearance of an IR absorption band corresponding to H=C=C stretching by FTIR spectroscopy. Finally, AgNW and UV curable PSA were mixed and coated to make a film. The sample was irradiated with UV through a mask to produce a pattern in which only the exposed portion to lost its adhesion. The adhesive portion was transferred to the opposite substrate through the stamping transfer process, and the sheet resistance was measured as nearly same to that before the transfer. Stretching and bending tests were performed on the fabricated samples, which demonstrated that they are well suited for the production of stretching electrodes.

EP04.08.05
A Hybrid PVDF/PDMS Electronic Skin for Accurate Touch Localization Keith Behrman, Caroline Yu, Pedro Placenza, Johnny C. Li, Matei Ciocarlie and Ioannis Kymissis; Columbia University, New York, New York, United States.

Flexible tactile sensors that can precisely and rapidly detect touch and provide location are of great importance for e-skin development [1]. Piezoelectric sensors are a great candidate because of their high voltage response, speed and sensitivity [2]. Current implementations use dense taxel arrays to accurately detect touch with high precision [3,4]. However, these solutions suffer from complex designs, slow response rates, expensive detection equipment or large wire arrays required to address individual sensors. The work presented here improves on current work by achieving high spatial resolution with a simple fabrication scheme and a minimal number of sensing elements. The sensing circuitry for the device utilizes a single charge-amplifier and a multiplexer controlled by a microcontroller to achieve high-speed measurements at a low cost.

Yu et al., have shown that multiple sensing modalities can be combined within a single PVDF sensor and utilizing compressible compliant layers, such as foam, can improve device sensitivity [5]. Here we iterate on this design by stacking two layers of PVDF with patterned electrodes to create a dense sensing area encapsulated and sandwiched by PDMS layers. The deformable nature of the PDMS offers increased sensitivity by acting as a compliant layer. PDMS can be used in a release mold to create a flexible skin that can be attached to existing grasping fingers, or the PDMS can be directly bonded to custom finger architectures to improve adhesion to the substrate while being fully integrated into the finger.

PVDF pre-coated on both sides with sputtered Cr/Au (40/250nm) was lithographically patterned and wet-etched utilizing backside alignment techniques to form electrode arrays
on a 15x15mm active area. The electrode arrays were electrically connected with heat-seal connectors before being stacked and encapsulated in PDMS. This sensor consists of two PVDF arrays with 16 electrode pairs to create a grid pattern. The electrodes were individually addressed with a multiplexer as seen in Geng et al., to simplify the circuit by using only one charge amplifier while maintaining a high sampling frequency [5].

The sensor was characterized with a robotic indenter by collecting individual sensor readings across a dense grid of indentation locations to train a kernel ridge regressor to predict locations against a test set of randomized locations. The prediction accuracy improves at deeper indentation depths and has a minimized prediction error of 0.78 mm with a standard deviation of 0.61 mm. Compared to a 15x15 array of individual taxels, this design achieves comparable spatial resolution with 14x fewer sensing elements. The sensor can also be implemented as a tri-modal sensor to capacitively sense object proximity, measure pressure by implementing strain gauges along with localization data from the grid. This rich information set can be used to augment robotic grasping applications.


EP04.08.06
Single-Crack-Activated Ultrasensitive Flexible Impedance Strain Sensor Iljong Ye; Mechanical Engineering, Tsinghua University, Beijing, China.

A development of single-crack-activated impedance strain sensors with unprecedented sensitivity is demonstrated first. The gauge factor of the device is beyond 10^6 in 10^4 strain range in comparison with the reported highest gauge factor 1.5 x 10^4 within 60% strain range, and the displacement sensitivity is 1.6 MΩ nm^-1. The extremely high sensitivity is attributed to the transition region which has never been studied before. Multiple crack-based sensors, however, cannot work in the transition region due to complicated interaction among cracks, which essentially limits their sensitivity. Additionally, studying a precisely controllable single crack rather than multiple cracks is favorable for excluding other factors such as crack spacing, difference among cracks, and interaction among cracks, simplifying the model and facilitating better understanding of the underlying mechanism of the device. The device can satisfy requirements of mechanical flexibility, durability, and repeatability. In addition, the device developed is capable of measuring displacement in nanometers range or force in tens of nanonewton range, and has the potential to be applied in various fields, such as specific biomolecular recognition.

EP04.08.07
Highly Stretchable Strain Sensors Comprising Double Network Hydrogels and Conducting Polymers Prepared by Microfluidic System Dowan Kim1, Jin-woo Oh2, Soo Hyung Kim2 and Jinhwan Yoon1; 1Graduate Department of Chemical Materials, Pusan National University, Busan, Korea (the Republic of); 2Department of Nanoenergy Engineering, Pusan National University, Busan, Korea (the Republic of).

Strain sensors with high sensitivity and stretchability are highly required for the application of wearable or implantable sensor to detect the human motion. In this study, we have prepared a highly stretchable double network (DN) of soft polyacrylamide and brittle calcium-alginate microfibers containing poly(3,4-ethylenedioxythiphene)-poly(styrene sulfonate) (PEDOT:PSS) by using microfluidic devices. The resistance changes in response to the stretching of the microfiber due to the connection/disconnection of the PEDOT:PSS domain can be observed up to 400% of elongation with the resolution of 0.1%. Furthermore, these changes are fully reversible and repeatable over more than 10,000 cycles at 300% elongation. On the basis of these mechanical and electronic properties, the DN microfibers are envisioned to use stretchable strain sensor, demonstrating the detection of the human motion including bending of the finger and walking and running in real time. We also demonstrated that the developed sensor can be stably used in outdoor by measuring the growth of the bamboo planted in the garden.

EP04.08.08
Fabrication, Characterization and Dielectric Spectroscopy of BaTiO3 Styrene Butadiene Styrene Stretchable Thin-Film Nanocomposites for Flexible Electronics Suporna Paul, Benard Kavey and Gabriel Caruntu; Central Michigan University, Mount Pleasant, Michigan, United States.

Polymer ceramic nanocomposites exhibit performance characteristics superior to those of the parent materials as they harness the electrical properties of the polymer and the dielectric properties of the ceramic. However, the rational design of flexible high-k dielectric nanocomposites with high filler loading is still challenging as the increase of the ceramic content deteriorates the mechanical properties of the nanocomposites. In this work, we investigated the fabrication of flexibleelectronics by dispersing BaTiO3 (BTO) colloidal nanocrystals with various sizes (10-20 nm) into the styrene butadiene styrene (SBS) matrix. The resulting SBS-BTO nanocomposite films contain up to 50% (weight) BaTiO3 nanocubes fillers and possess high energy density values along with excellent mechanical properties. It has been observed that the nanocomposite films can easily be peeled off from any type of substrate which is an indication of good flexibility and strength of these free standing films. We observed a linear increase in the dielectric constant with respect to fillers content, ranging from 6.1 to 24.1 for 0% to 40% respectively. The alternate current (AC) conductivity of the polymer remained below 10^-8, which shows the polymer is insulative and can be used in flexible capacitor applications. Also, with scanning electron microscope, we observed that, the BTO colloidal nanocrystals are uniformly distributed in the polymer matrix which can explain the reason behind of good flexible property of the film. The experimental results show that these nanocomposite thin films exhibit superior properties which make them attractive for implementation in high-performance capacitive storage devices, wearable technology and nanoelectronics.

EP04.08.09
Transformable Crystalline Silicic Photovoltaics Inchan Hwang and Kwanyong Seo; UNIST, Ulsan, Korea (the Republic of).

Transformable photovoltaics (TPVs) have been attracting much attention because of the limitation of the PV’s installation and a continuous power source for the portable and wearable electronic devices. At present, TPVs have been developed based on the perovskite and organic photovoltaics. However, these PVs have problems of the low efficiency and instability. In contrast, crystalline silicon (c-Si) PVs exhibit high efficiency and stability, but they are not able to be transformable because they tend to be fragile when an external force is applied. Therefore, a new strategy for the TPVs technology based on the crystalline silicon is required to realize the high efficiency and stable c-Si TPVs. In this research, we developed the c-Si TPVs through the interdigitated back contact (IBC) structured c-Si module and introduction of a stretchable electrode. Because all electrodes (positive and negative contact) of the IBC PVs are positioned on the rear side, we can easily fabricate the TPVs module using the stretchable electrode. The stretchable electrode is consisting of the combination of the carbon materials and elastic polymer. The stretchable carbon filler/ polymer composite is found to effectively retain its electrical conductivity, even when under the high strain of ≥200%. Due to the outstanding electrical conductivity and highly stretchable property of the carbon filler/ polymer composites, the fabricated IBC PVs can be transformable without the efficiency degradation. Thus, we expect that the proposed c-Si TPVs are possible to overcome the PV’s installation limitation and integrate with flexible or wearable electronic devices for the continuous power source.

EP04.08.10
Effective Processing Strategies to Integrate Ag NWs with Polymer Semiconductors for High Performance Stretchable Field Effect Transistors Rujiao Song1, Shanshan Yao1, Zheng Cui1, Jingyan Dong2, Yong Zhu1 and Brendan T. O’Connor1; 1Mechanical & Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2Industrial & Systems Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Intrinsically stretchable transistors are a critical building block for an array of stretchable electronic applications. They also represent a model system where conductors, semiconductors, and insulators must all be stretchable and effectively integrated. Here, we present an intrinsically stretchable organic field effect transistor that incorporates Ag nanowires (NWs) as the source, drain, and gate electrode with a stretchable PDMS gate dielectric and stretchable DPP-4T polymer semiconductor. The Ag NWs provide a significant improvement in electrical conductivity compared to other candidate stretchable electrode materials such as carbon nanotubes and PEDOT:PSS. However, there are several challenges associated with roughness and patterning that can limit their application. Here, we demonstrate an effective processing strategy of embedding the Ag NWs in a PDMS elastomer allowing for high stretchability and high conductivity. This high conductivity enables the electrical leads and electrodes to be composed of the same material. The NWs are patterned using direct electrophyssohydrodynamic jet printing, and through drop casting followed by laser ablation. While the NWs are embedded in the elastomer, we show that the surface of the NW network is able to effectively contact the semiconductor for low contact resistance transistor performance. Through this processing strategy we are able to demonstrate a stretchable transistor with a saturated field effect mobility that remains largely unchanged when under an applied strain of 40%, and remains functional under cyclic loading. As part of this work, the morphology of each active component is studied in detail along with detailed device characterization.
Flexible and Multi-Functional Energy Storage Devices with High Safety

Yang Zhao, Ye Zhang, Yifan Xu, Hao Sun and Huisheng Peng; Fudan University, Shanghai, China.

Flexible energy storage devices are critical for the next-generation electronics and have attracted extensive attention. With the fast-growing requirements of portable and wearable electronic equipment, great efforts have been made to develop flexible batteries and supercapacitors. However, the energy densities of these devices are still urgent to be further increased. Furthermore, most of the reported flexible batteries and supercapacitors employ either strong acid/base or toxic flammable organic solutions as electrolytes, which poses potential safety issue for being worn by humans or implanted into the bodies. Therefore, the energy density, safety concerns and compatibility of the flexible energy storage devices are still urgent to be improved to meet the practical application requirements.

Herein, we have developed a new family of flexible energy storage devices including fiber-shaped aluminum-air battery with superior energy density, self-healing and multi-functional aqueous batteries with high safety, and a novel sticky-note supercapacitor with high compatibility. 1. The all-solid-state fiber-shaped aluminum-air batteries showed a specific capacity of 935 mAh/g and an energy density of 1168 Wh/kg. They are also flexible and stretchable and can be further woven into a variety of textiles. 2. After breaking, the flexible self-healing batteries can be healed to recover the normal functionality by simply contacting the two breaking parts for seconds. The electrochemical performance of these batteries can be well maintained after repeated cutting and self-healing. 3. The flexible aqueous sodium-ion batteries exhibit high volumetric energy/power density and high flexibility. When the normal saline or cell culture medium is used as electrolyte, these batteries can still work well, indicating an application prospect in implantable electronic devices. 4. The sticky-note supercapacitor demonstrated high compatibility and can be easily and repeatedly attached onto various substrates including cloth, glass, paper, plastic and metal with the electrochemical performance well maintained. These flexible and multi-functional energy storage devices can be woven into lightweight and flexible electronic textiles to effectively meet the requirement of the modern electronics including portable and wearable products.

Bioinspired Multi-Responsive Soft Actuators Controlled by Laser Induced Graphene

Heng Deng, Cheng Zhang, Jhong-Wun Su, Yunchao Xie, Chi Zhang and Jian Lin; University of Missouri, Columbia, Missouri, United States.

By exploiting aligned cellulose fibrils as geometrically constraining structures, plants can achieve a complex programmable shape change in response to environmental stimuli. Inspired by this natural prototype, a series of manmade materials with aligned structures have been developed and employed in self-morphing materials. However, in these cases, the constraining materials are fabricated and aligned in separate processes. In botanic systems, a more efficient way is adopted, in which the aligned microstructures are simultaneously synthesized and aligned in one bottom-up process. Herein, we report a bioinspired bottom-up approach to fabricate laser induced graphene (LIG) structures which resemble the aligned microstructures of the cellulose fibrils in plants. Such LIG structures serve as geometrically constraining structures to precisely control the shape-changing behaviors of soft actuators made from polymer and LIG layers. Meanwhile, the LIG structures also serve as functional materials to absorb photo and electrical energy to stimulate motions of the soft actuators. Taking advantage of the geometrically constraining effect from the aligned LIG structures, a series of programmable actuations stimulated by electricity, light, organic vapor, and moisture were demonstrated. Furthermore, the soft actuators also act as soft grippers and walking robots upon different stimuli, indicating their potential applications in soft robotics, electronics, microelectromechanical systems, and others.

Robust and Stretchable Polymer Semiconducting Networks—From Film Microstructure to Macroscopic Device Performance

Guoyan Zhang and Elsa Reichmanis; Georgia Institute of Technology, Atlanta, Georgia, United States.

Although stretchable polymer-based devices with promising electrical performance have been produced through the polymer blend strategy, the interplay between the blend film microstructure and macroscopic device performance under deformation has yet to be unambiguously articulated. Here, we will discuss the formation of robust semiconducting networks in blended films from a thermodynamic perspective. Thermodynamic behavior along with the linear absorption and photoluminescence measurements predict the competition between polymer phase separation and semiconductor crystallization processes during film formation. Semiconducting films comprised of different pi-conjugated semiconductors were prepared and shown to have similar mechanical and electronic properties to films comprised of a model P3HT and PDMS blend. These results suggest that a film’s microstructure and therefore robustness can be refined by controlling the phase separation and crystallization behavior during film solidification. Fine-tuning a film’s electrical, mechanical, and optical properties during fabrication will allow for an advanced next-generation of optoelectronic devices.

Stretchable/Flexible Transparent Conductors for Emerging Optoelectronic Devices and Epidermal Transducers

Bin Hu; Huazhong Univ of Science and Technology, Wuhan, China.

Compared with continuous transparent conductive films, such as metal oxides that cannot effectively release the strain during bending or stretching, percolated network composed by conductive nanowires like silver nanowires (AgNWs) can be a ductile form, which also possesses excellent electro-optical performance and solution-processed manufacturing. However, this unique metal percolated structure also has issues, such as the binding strength with polymers and poor patterning performance. Therefore, the design of network and development of compatible techniques become important for practical applications in stretchable/flexible optoelectronic devices.

In our study, we firstly use finite element simulation to explore the electrical, optical and mechanical properties of the network, which guides us to optimize the fabrication of stretchable polymer-based devices with promising electrical performance. 1. The all-solid-state fiber-shaped aluminum-air batteries showed a specific capacity of 935 mAh/g and an energy density of 1168 Wh/kg. They are also flexible and stretchable and can be further woven into a variety of textiles. 2. After breaking, the flexible self-healing batteries can be healed to recover the normal functionality by simply contacting the two breaking parts for seconds. The electrochemical performance of these batteries can be well maintained after repeated cutting and self-healing. 3. The flexible aqueous sodium-ion batteries exhibit high volumetric energy/power density and high flexibility. When the normal saline or cell culture medium is used as electrolyte, these batteries can still work well, indicating an application prospect in implantable electronic devices. 4. The sticky-note supercapacitor demonstrated high compatibility and can be easily and repeatedly attached onto various substrates including cloth, glass, paper, plastic and metal with the electrochemical performance well maintained. These flexible and multi-functional energy storage devices can be woven into lightweight and flexible electronic textiles to effectively meet the requirement of the modern electronics including portable and wearable products.

References


Fully Printed Carbon Nanotube Network Thin-Film Transistor Based Gas Sensors on Flexible Substrates

Diego Vaca, Jiakuo Chen, Woonhong Yoo and Satish Kumar; School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 3Petit Institute for Bioengineering & Bioscience, Georgia Institute of Technology, Atlanta, Georgia, United States; 4W. W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 5Wallace H. Coulter Department of Biomedical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Aerosol jet printing (AJP) has been proven to be capable of printing microelectronic devices and relevant circuits with relatively high precision, repeatability, and scalability using a wide range of materials because it can handle inks viscosities in the range of 1-1000 Cp. In this work, fully-printed thin film transistors (TFTs) have been fabricated on flexible films microstructure and therefore robustness can be refined by controlling the phase separation and crystallization behavior during film solidification. Fine-tuning a film’s electrical, mechanical, and optical properties during fabrication will allow for an advanced next-generation of optoelectronic devices.
substrates. Metallic, semiconducting, and dielectric materials such as silver, single walled carbon nanotubes (SWCNTs), and xdi-dcs, have been printed successively with high quality using APJ. In this fabrication process, CNT network is printed in the channel region of TFTs as a semiconducting CNT solution. Highly uniform CNT network film is achieved by performing a multiple layer-by-layer deposition method. The printing of thin layer of xdi-dcs as gate-dielectric is realized by diluting with n-butanol solvent and plasma treatment for better surface wetting during printing. Fully printed CNT-TFTs showed a very stable performance with on/off current ratio as high as ~10^8, mobility around 5 cm^2V^{-1}s^{-1}, negligible hysteresis, and good uniformity. More importantly, this device can be operated using bias voltages as small as 5V, which is much smaller than the previously reported values because of the improvement in both CNT network and dielectric layer (thicker). CNT-TFTs were used as gas sensors to detect NO_2 and NH_3 and their performance was compared with two-electrode CNT gas sensors. Our printing method has potential to further reduce the bias voltages for operation. This improvement is key for the application of printed microelectronics and CNT-TFTs based circuits on flexible substrates because of the relatively lower voltage operation and power dissipation.

EP04.08.17
Water Permeable Sticky Patch with Serpentine Patterns for Detection of Electrophysiological Signals
Hyeokju Chae, Sunkook Kim, Srinivas Gandla and Muhammad Naqvi; Advanced Material and science, Sungkyunkwan University, Suwon, Korea (the Republic of).

Skin patch based stretchable sensors for Physiological monitoring have drawn great attention due to their significant finding in many human-machine interaction applications. As of now, stretchable serpentine structures supported by biocompatible elastomeric substrates have been widely examined for conformable and strain relief stretchable electrophysiological sensors. However, the substrates are not breathable, which is crucial for next-generation wearable electronics. Additionally, the fabrication of these sensors mostly relies on conventional lithographic techniques followed by etching processes that are complex, expensive and entail multiple steps, which greatly impede the realization of low-cost and scalable manufacture electronics. The development of flexible stretchable materials and novel processing techniques can enable a viable solution for these electronics.

In this, we present a novel low-cost and rapid “cut and transfer” method to fabricate electrophysiological sensor using a benchtop programmable mechanical cutter plotter. Furthermore, the stretchable sensor performances have been achieved by introducing a water permeable patch possessing filamentary serpentine patterns that are stretchable, sticky, and conformable. Moreover, the sensors maintain the sensing performances irrespective to the deformations that are imposed. Overall, the fabrication method offers the chance of developing a new format of stretchable and flexible electronics.
communication through a recyclable on-board computation unit. Such advances in the synthesis of biodegradable, mechanically tough and stable ionico-and hydrogels may bring bionic soft systems a step closer to nature.

9:30 AM EP04.09.04
Programmed Mechanically-Triggered Ultrafast Soft Robots for Implantations Beyond Human

Soft robots have been designed and developed to fulfill the demands of better deformability and adaptability to changing environment [1-2]. These soft robots could be made of various stimuli responsive materials that can be actuated by magnetic field [3], light [4], temperature [5], electric fields [6], chemicals [7], pressure [8], etc. In contrast to other actuation mechanisms, magnetic fields are appealing for numerous application scenarios (e.g. environmental, biological, medical), where the benefits stem from their long-range penetration, easy accessibility, and controllability of magnetically triggered millimetre- and centimetre- scaled soft robots performing multimodal locomotion [9] and complex 3D actions [10]. However, their thick and bulky bodies [9-10] challenge themselves to reveal better performances for specific implantations which require more, for instant action speed, and reversible large-scale actuation amplitude by a rather low magnetic field.

Here, we present an ultrathin (7-100 μm) and lightweight (1.2-2.4 g/cm3) soft robot that can be actuated in a tiny magnetic field of 0.2 mT reaching full action amplitude with a reaction time of 10 ms only. By programming the foils into different geometries, these soft robots are readily used for multifunctional nature-mimicking motion with a magnetic coil or a permanent magnet, such as a quick fly gripping and releasing, complex fast human cross-clapping mimicking, etc.


9:45 AM BREAK

10:15 AM *EP04.09.05
Organic Haptics
Darren J. Liponi1; University of California, San Diego, La Jolla, California, United States.

The goal of this project is to create a class of electronic materials that can measure signals and interface with the nervous system for two-way communication with biological systems. The project is exploring three classes of materials. (1) Semiconducting polymers with properties inspired by biological tissue. The goal of organic bioelectronics is to detect and treat disease by using signal transducers based on organic conductors and semiconductors in wearable and implantable devices. Except for the carbon framework of these otherwise versatile materials, they have essentially no properties in common with biological tissue: electronic polymers are typically stiff and brittle, and do not degrade under physiological conditions. Such properties can be realized in a single-component polymer by incorporating biocompatible subunits. We have synthesized a new type of stretchable, biodegradable polymeric semiconductor whose electronic performance is unaffected by the biodegradable components. Such materials have applications in wearable and implantable sensors. (2) Metallic nanoislands on single-layer graphene for cellular biomechanics and wearable sensors. We have used these materials to measure the forces under physiological conditions. Such properties can be realized in a single-component polymer by incorporating biocompatible subunits. We have synthesized a new type of stretchable, biodegradable polymeric semiconductor whose electronic performance is unaffected by the biodegradable components. Such materials have applications in wearable and implantable sensors. (3) Ionically conductive organogels for haptic feedback. Medical and implantable sensors. (2) Metallic nanoislands on single-layer graphene for cellular biomechanics and wearable sensors. We have used these materials to measure the forces under physiological conditions. Such properties can be realized in a single-component polymer by incorporating biocompatible subunits. We have synthesized a new type of stretchable, biodegradable polymeric semiconductor whose electronic performance is unaffected by the biodegradable components. Such materials have applications in wearable and implantable sensors.

10:45 AM EP04.09.06
Tattoo-Like Electronic Systems for on Body Measurements
Andrea Spanu1, Danilo Pani2, Andrea Achilli2, Fabrizio Viola2, Annalisa Bonfiglio3, and Piero Possad4; 1MST-Microsystems Technology CMM-Center for Materials & Microsystems, FBK-Bruno Kessler Foundation, Trento, Italy; 2Università Degli Studi di Cagliari, Cagliari, Italy; 3Istituto Italiano di Tecnologia, Milano, Italy.

The recent rise of the so-called “tattoo electronics” has pushed further the innovation on flexible and ultra-conformable electronic devices that can be transferred onto the skin, being this unprecedented possibility of obtaining a seamless skin/electronics interface particularly interesting for biomedical imaging. In fact, these systems can be specifically engineered in order to adhere to the skin and they could include several kinds of electronic devices, such as sensors, light-emitting diodes, photodetectors or electrodes for biopotentials acquisition. In this work, we have developed a very simple approach for the realization of ultra-conformable electronic systems, such as electrodes and sensors that can be employed for the recording of biopotentials and/or different physiological parameters.

The proposed approach is based on the employment of a nanometric film of Parylene C. The process starts from a plastic substrate on which we spin coat a sacrificial layer which can be dissolved in either polar or non-polar solvents. After that, a submicrometer film of parylene C is deposited, such nano-films acting as the actual substrate where electrodes for biopotential acquisition and OTFT-based sensors can be fabricated using standard techniques (such as, for example, photolithography, micro-contact printing, and inkjet printing). Once the fabrication process is completed, the sacrificial layer can be dissolved allowing the electrodes/sensors to be easily transferred onto a different substrate, as for instance onto the skin.

In this work we report about the employment of such tattoo electrodes for the recording of both electrocardiographic (ECG) and electromyographic (EMG) signals, which can be performed standard commercial pre-gerellated electrodes in terms of signal-to-noise-ratio and movement artifacts suppression. Moreover, a particular kind of organic transistor sensor called organic charge-modulated field-effect transistor (OCMFET) has been fabricated onto such nanometric thin films and coupled to a solution processable and printable piezoelectric/pyroelectric polymer, namely PVDF-TrFE, in order to obtain ultra-thin multimodal force and temperature sensors. Such devices can detect very small pressure (below 300 Pa) in both the static and the dynamic regime, being in fact able to detect stimuli at a frequency enough to 500 Hz. Moreover, thanks to the pyroelectric properties of PVDF-TrFE, temperature variations ranging from 10 °C up to 45 °C can be also detected. Interestingly enough, we will show that with the proposed approach it is also possible to employ the same device and the very same active layer for the fabrication of multimodal tactile sensing systems. The highly flexibility of the developed structure and the simple fabrication process make this solution a very interesting candidate for the development of ultra-sensitive, multimodal, and mechanically compliant electronic systems that can be employed in many different scenarios, ranging from biomedical applications to robotics and prosthetics.

11:00 AM EP04.09.07
Electro-Active Soft Photonic Devices for the Simultaneous Generation of Color and Sound
Do Yoon Kim1, Sunglok Choi2 and Jeong-Yun Sun1; 1Seoul National University, Seoul, Korea (the Republic of); 2Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of).

For the satisfactory fulfillment of the two primary human senses (i.e., vision and hearing), every contemporary media platform employs an independent speaker and display, as display panel technology currently disallows tunable audio-frequency vibration. However, mechatronic systems that feature amenability towards color tuning based on structural deformation have an inherent potential for the generation of mechanical vibration; all the same, most systems are constrained to demonstrations in low-frequency regimes (< 1 Hz) as color change events necessitate large strains, which has until now precluded the possibility for simultaneous high-frequency vibrations. It is well known that overcoming sluggish strain response rates that are characteristic of stretchable viscoelastic material systems is extremely challenging. Hence, most mechatronic systems have thus far only aimed at satisfying visual perception and have overlooked the possibility of a merger of sound and display modules, despite their disparate inherent mechanical vibration modes. Here, we target both senses, especially under single input control by actuating a single mechatronic platform built from an organogel skin composed of close-
packed photonic lattices with an organogel matrix. Exploiting a dielectric elastomer actuator, the skin features large areal strains at low frequencies of actuation, which allows the reversible tuning of the photonic stop-band. Notably, the skin remains incompressible and exhibits negligible strain when actuated at higher frequencies (e.g., audio frequencies), thereby making it amenable for sound modulation in this regime. Remarkably, a pseudo-synthetic event with color and sound can be orchestrated with a single actuation mode; that is the simultaneous generation of the large strain (for color) with the high-frequency vibration (for sound) by taking advantage of the soft and highly responsive photonic organogel skin. This strategy will be widely helpful to eliminate the need for the independent construction of modules for color and sound, as required in all current commercial implementations. The evolution of flexible electronics has enabled the appearance of revolutionary concepts like electronic skins (e-skins) [1-3], wearable electronics and smart implants, among others. E-skins have the potential to seamlessly integrate with the human body owing to their mechanically imperceptible and compliant nature. Due to these characteristics, they provide a much more natural way of interacting with electronic devices by eliminating the need for bulky or stiff parts interfering with human perception. Furthermore, conventional flexible interactive electronics typically use tactile stimuli like pressure or temperature [4,5], limited to direct contact detection. To progress beyond tactile approaches, we have recently demonstrated magnetosensitive skins [7-12] as a touchless alternative for interactivity. These skins can utilize a plethora of magnetic stimuli like permanent magnets [7-10], the geomagnetic field [11] and even submicrotesla fields [12], to reconstruct and digitize spatial interactions. Here, we present the technologies at the core of these interactive magnetosensitive skins and showcase some of the applications stemming from them [10-12]. These technologies utilize different configurations of magnetoresistive (MR) and planar Hall-effect sensor elements, based on metallic thin films fabricated on 6-µm-thick polymeric foils. The combination of this broad spectrum of sensors allows multiple magnetic range detection possibilities for these magnetosensitive skins. Besides, by introducing geometrical conditioning like barber poles [13] or measurement schemes like zero-offset anomalous Hall magnetometry [14,15], the output sensitivity and offset can be tuned to increase the overall performance. We anticipate that this novel kind of magnetic skins could be used to track and digitize fine motion in an ultra-thin and lightweight format. This feat could ease the integration of usually rigid magnetic detection systems into on-skin, textile-based or Internet of Things (IoT) applications. A successful implementation could lead to a new class of virtual or augmented reality systems and interactive input devices which extract information from their surroundings through magnetic signals.

SESSION EP04.10: Soft and Stretchable Systems and Applications II
Session Chairs: Roozbeh Ghaffari and Cunjiang Yu
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 222 A

1:30 PM *EP04.10.01
Soft and Ultra-Conformable Electronic Circuits on Thin Metallic Foil Séverine C. de Mulatier1,2, David Coulon2, Sylvain Blayac1, Roger Delattre1 and Marc Ramuz1; 1Department of Flexible Electronics, Ecole Supérieure des Mines de Saint-Etienne, Centre Microélectronique de Provence, Gardanne, France; 2@-HEALTH, Aix-en-Provence, France.

Fabrication of complex circuitry for ultra-conformable and imperceptible devices is a key challenge for tomorrow-wearable technologies. As a matter of facts, the only way today to perform complex computational operations, such as data processing and transmission, is by using standard rigid silicone-based systems. The mismatch in mechanical properties between conformable substrates and rigid components induces specific reliability issues, especially for wearable systems, as they are subjected to wearing and washing.

In this work, we focus on different solutions to create thin and ultra-conformable electronic circuit, using a customized stack of thin metallic foil on a polymer film. We consider and study the aforementioned aspects of imperceptibility (wearability) through conformability, and robustness through specifically designed bending and washing tests. This study investigates the optimization of electrical connection between ultra-soft substrates and rigid components, and the influence of the stack composition in multilayer electronic systems on the overall reliability of the device.

The combination of optimized stack layout and compliant interconnections allow the fabrication of robust and ultra-conformable, imperceptible devices.

2:00 PM EP04.10.02
Flexible and Wearable Electronics Based on 2D Materials Jong-Hyun Ahn; Electrical and Electronic Engineering, Yonsei University, Seoul, Korea (the Republic of).

With the emergence of unusual format electronics such as flexible and wearable devices, an effort has been made to integrate devices with various functions in smart clothing and human body for providing enhanced convenience for the users. However, it is difficult to accomplish such emerging electronics with conventional rigid inorganic materials. Two-dimensional (2D) materials such as graphene and transition metal chalcogenides have superb electronic properties that make them a promising host for device applications and they are increasingly studied for the next generation electronics.

In this talk, we focus on the development of flexible electronics using two-dimensional materials such as graphene and transition metal chalcogenides for applications in energy harvesting and biomedical devices. The design and fabrication of graphene and transition metal chalcogenides-based devices are discussed with their potential applications.

2:15 PM *EP04.10.03
Climbing-Inspired Twining Electrodes Using Shape Memory for Peripheral Nerves Stimulation and Recording Xue Feng and Yinji Ma; Department of Engineering Mechanics, Tsinghua University, Beijing, China.

Peripheral neuromodulation has been widely used throughout clinical practices and basic neuroscience researches. However, the mechanical and geometrical mismatch in the current electrode-nerve interfaces, and the complicated surgical implantation often induce irreversible neural damages such as the axonal degradation. Here, compatible with the traditional 2D planar processing, we propose a 3D twisting electrode by integrating stretchable mesh-serpentine wires onto flexible shape memory substrate, which possesses shape re-configurability (from 2D to 3D), distinct elastic modulus controllability (from ~100MPa to ~300kPa) and shape memory recoverability at body temperature (~37°C). Similar to the climbing process of twining plants, the temporarily flattened 2D stiff twisting electrode can naturally self-crimp onto nerves driven by 37°C normal saline, and forming 3D flexible neural interfaces with minimal restraint on the deforming nerves. In vivo animal experiments including the right vagus nerve stimulation for the heart failure therapy and the action potential recording of the sciatic nerve for the neuroprosthetics demonstrate the potential clinical utility.

2:45 PM BREAK

SESSION EP04.11: Wearable Sensors and Devices
Session Chairs: Roozbeh Ghaffari and Cunjiang Yu
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 222 A

3:15 PM *EP04.11.01
Flexible and Wearable Electronics Based on 2D Materials Jong-Hyun Ahn; Electrical and Electronic Engineering, Yonsei University, Seoul, Korea (the Republic of).

With the emergence of unusual format electronics such as flexible and wearable devices, an effort has been made to integrate devices with various functions in smart clothing and human body for providing enhanced convenience for the users. However, it is difficult to accomplish such emerging electronics with conventional rigid inorganic materials. Two-dimensional (2D) materials such as graphene and transition metal chalcogenides have superb electronic properties that make them a promising host for device applications and they have a good mechanical property, offering a great opportunity to flexible and wearable electronics that should maintain a stable operation under a high strain. In this talk, I will present various flexible and wearable electronic applications for including touch and self-powered communication devices, and biosensors.

3:45 PM EP04.11.02

The extraneous thermal regulation of the human body has a wide array of applications ranging from assisting with medical conditions such as Multiple Sclerosis (MS) to being an essential component in the design of protective suits used for maneuvering extreme environments. Out of the plethora of thermoregulatory garment designs that are available commercially or have been proposed in the literature, liquid-cooled garments provide one of the highest heat removal capacities along with sustained and nearly-environment independent performance. In addition to the thermal regulation of the human body, these liquid-cooled garments show potential to meet the rising demand to dissipate the heat produced by wearable electronics and high power robotics while maintaining the sought after flexibility. However, in these thermoregulatory liquid cooled garments the tubing
material often used is rigid PVC which has a very low thermal conductivity, of around 0.2 Wm⁻¹K⁻¹; a value far too low to effectively deal with the amount of heat that will inevitably be generated by future wearable electronics. A low thermal conductivity contributes to magnifying the total thermal resistance which results in an excessive amount of tubing being networked around the human body or electronic device to effectively regulate its temperature. This excessive amount of tubing in turn has to be carried around by the wearer.

In this work, we explore how tubing made of soft, thermal conductive elastomers composites can improve on the performance of these liquid-cooled jackets (LCJ). In doing so, we study the effect of filler material on the tube-wall thermal resistance in combination with the interfacial thermal resistance. The interfacial resistance depends on mechanical properties of the materials in contact, thus, a microscale composition of the filler particles and matrix elastomer that provides a balance between thermal and mechanical properties of the composite must be achieved for optimal performance of the cooling device. To explore this relationship, we develop a closed-form thermomechanical model that predicts thermal performance of a composite silicone LCJ as a function of metallic filler content. To validate the model, we fabricate a set of liquid-cooled jackets out of silicone-aluminum composites. We relate the cooling ability of these devices with composition as well as thermal and mechanical properties of the composite materials. Based on these results, we develop LCJ architectures with material properties tuned via composition adjustment at each device level to achieve optimal device performance for personal (skin substrate) and robotic (metal substrate) cooling.

4:00 PM EP04.11.03
Point-of-Use Flexible Sensors for Health and Environmental Applications—Assessment of Motor Skills and Chemical Exposure Moran Amit1, Sarah Hacker2,3, Trent Simmons2,3, Rupesh K. Mishra1, Quyen Hoang1, Aida Martin Galan1, Leanne Chukoskie2,3, Joseph Wang1 and Tse Ng Ng1,2,3,4,5,6; Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, California, United States; Institute for Neural Computation, University of California, San Diego, La Jolla, California, United States; Research on Autism and Development Laboratory (RAD Lab), University of California, San Diego, La Jolla, California, United States; Department of Nanoengineering, University of California San Diego, La Jolla, California, United States.

Rapid, on-site assessment is highly desirable in the fields of both medical treatment and novel robotics. To achieve this goal, our research aims to develop low-cost, flexible, large-area sensor devices for different health and environmental applications. In this presentation, we discuss case studies using touch and pressure sensors for two different point-of-use applications:

I) Autism spectrum disorder (ASD) motor skills characterization. There is no objective metric for evaluating motor skill training progress in autistic children, and current assessments rely on qualitative surveys. A common method used is a finger tapping task that requires videotaping and unreliable, time-consuming manual analysis, with large room for errors, even with computer vision analysis algorithms. We have fabricated an instrumented glove with touch sensors on textile for straightforward finger tapping patterns characterization. The results provide immediate objective feedback not only on the tapping counts, but on the temporal data (such as tapping duration and variation in duration) as well, which was not collected before. For the index finger tapping test, children with ASD perform less counts per minute compare to typically developing (TD) children. In addition, children with ASD tap their finger for an average longer duration, with larger variation between tap durations. In a 4-fingers tapping test children with ASD tend to have more irregular patterns and skip fingers compared to TD children. This glove could find future use for characterizing motor skills of people suffering from Parkinson’s disease, epilepsy seizures, and other neurological motor disorders.

II) Robotic sensors for simultaneous pressure and organophosphate (OP) pesticide detection. There is an urgent need of sensor technologies to monitor hazardous materials for security and environmental applications, in particular, the occurrence of OP pesticide residues in agricultural products that poses a serious concern in the food and agriculture industries. Hence, rapid on-site detection of OPs through remote robotic sampling is highly desired to avoid placing people at exposure to the OPs risks. To handle sample collection, the robotic manipulator requires tactile feedback, in order to ensure no damage will be done to either the robot or the other object in contact due to excessive force. To provide tactile feedback, pressure sensors based on capacitive mechanism were chosen. The sensitivity of the capacitive pressure sensors was tuned by adjusting the dielectric compressibility. Particularly, the sensitivity was increased by choosing softer materials, i.e. elastomers with low elastic modulus and porous structure that further lower elastic moduli of the foam dielectrics compared to solid films of the same material. We have combined low-cost chemical and pressure sensors together on disposable gloves, and demonstrated successful simultaneous tactile sensing and OP pesticide detection in a point-of-use platform that is scalable and economical.

4:15 PM EP04.11.04
All Stretchable Aqueous Rechargeable Batteries for Wearable Devices Woo-jin Song and Soonjip Park; Chemistry, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

There is currently a great deal of interest in stretchable electronics for widespread applications such as wearable devices, smart sensors, healthcare devices, electronic skins, and soft robotics. The stretchable electronic devices that consist of soft and deformable components can stably maintain their functions under the complex physical deformations such as bending, twisting, folding, and stretching. To achieve independent and reliable stretchable electronics, a key challenge is the development of stretchable energy-storage devices that could power such devices. Among them, Li-ion batteries (LiIBs) is a representative power source for the portable electronics owing to their advantages such as high working voltages, stable cycle life, and high energy density. However, LiIBs are based on a volatile and flammable non-aqueous electrolyte, which make them a high risk of explosion owing to the internal short circuit during extremely mechanical deformations. For this reason, typical LiIBs are not suitable for energy storage-devices system in stretchable electronic devices. Compared with LiIBs, aqueous rechargeable batteries hold great potential for a power supply in stretchable electronics because of the aqueous electrolyte having inherent safety features and high ionic conductivity. Herein, we successfully replaced rigid components of typical batteries including, electrodes1 and a separator membrane2, with stretchable materials using straightforward and scalable fabrication strategies. First, we fabricated a conductive polymer composite composed of bio-inspired Jabuticaba-like hybrid carbon/polymer (HCP) composite as a stretchable current collector, which effectively maintained its electrical percolation network even under 200% uniaxial strain. To further understand the behavior of carbon fillers in the polymer matrix under strain. And then, a poly(styrene-b-butadiene-b-styrene) (SBS) block copolymer-based stretchable separator membrane was fabricated by the nonsolvent-induced phase separation (NIPS). The diversity of mechanical properties and porous structures can be obtained by using different polymer concentration and tuning the affinity among major components of NIPS. The stretchable separator membrane showed a high stretchable feature (~270% uniaxial strain) and porous structure (~61% porosity). Using as-prepared the stretchable electrode and the stretchable separator membrane, we assembled stretchable aqueous Li-ion batteries as a power source for use in stretchable electronic devices. As a result, our all stretchable aqueous batteries manifested good cycling performance and stable capacity retention even under 100% uniaxial strain, without failing the battery performance.

1) Song et. al, Advanced Energy Materials, 2018, 8, 1702478
2) Song et. al, Advanced Energy Materials, 2018, 8, 1801025

4:30 PM EP04.11.05
Addressable Organic Light-Emitting Diode Fabrics Toward Fully-Functional Wearable Displays Young Jin Song, Jae-Won Kim, Ha-Eun Cho and Sung-Min Lee; Kookmin University, Seoul, Korea (the Republic of).

To expand the application area, unconventional forms of displays have been actively emerging beyond the flexible displays. The wearable display is conceded as one of the promising forms of such unusual emerging displays due to its remarkable functions such as real-time communication and superior portability. The wearable cloth-type displays are particularly imperative in the commercial fields because of their notable contribution to offering a high degree of freedom in terms of design and functions. There have been successful demonstrations of the so-called ‘on-cloth’ displays, where textiles (i.e. woven fabrics) were instead used as substrates of the devices. Without technical issues in defining a two-dimensional pixel matrix and making their interconnections, the reported systems of the on-cloth displays could work as fully-operating display panels. On the other hand, current technology for the ‘on-cloth’ displays that comprise emitting fibers is limited to a level of the lightings rather than the information displays, as there has been a hurdle to form a two-dimensional interconnection network with one-dimensionally configured fibers, and hence no route to perform the matrix addressing for driving designated pixels. In this regard, here we present a highly feasible approach to achieve the on-cloth class of matrix-addressable displays by weaving assembly with perpendicularly arranged organic light-emitting diode (OLED) fibers and conducting fibers. To create the OLED fibers that behave as scan lines of the matrix addressing, periodically patterned phosphorescent OLED pixels are thermally deposited on polyethylene terephthalate (PET) fibers coated with indium tin oxide (ITO) common electrodes, where complete passivation of the deposited organic constituents and subsequent formation of contact pads connected to the top electrodes of each OLED pixels are implemented to prevent the mechanical damage to the pixels as well as the water/oxygen permeation. The contact pads of OLED pixels on the OLED fibers can be electrically linked to the other perpendicular conducting fibers of data addressing lines by simply tailoring cross spots of layout design, which allows the successful operation of the resulting woven OLED fabric displays by the matrix addressing scheme. Details of fabrication strategy to enhance the reliability of matrix-addressable OLED fabric displays can provide technically compelling solution options for

**Session Chairs:** Pooh See Lee and Marc Ramuz

**Friday Morning, April 26, 2019**

**PCC North, 200 Level, Room 222 A**

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**8:00 AM EP04.12.01**

**Emerging Designs for Polymer-Based Infrared Photodetectors**

Zhenghui Wu¹, Weichuan Yao¹, Hyunwoong Kim¹, Yichen Zhai², Jason Azoulay² and Tse Nga Ng¹;¹University of California, San Diego, La Jolla, California, United States; ²University of Southern Mississippi, Hattiesburg, Mississippi, United States.

The shortwave infrared spectral region (SWIR: 1-3 um) is particularly powerful for health monitoring and medical diagnostics, because biological tissues show low absorbance and minimal SWIR auto-fluorescence, enabling greater penetration depth and improved resolution in comparison to visible light. However, current SWIR photodetection technologies are largely based on epitaxially grown inorganic semiconductors which are costly, require complex processing and impose cooling requirements incompatible with wearable electronics. Organic semiconductors offer numerous advantages including large-area and conformal coverage, temperature insensitivity, biocompatibility, and low-cost integration for enabling ubiquitous SWIR optoelectronics. This talk will discuss organic SWIR devices and discuss the main bottlenecks associated with charge recombination and trapping, which are more challenging to address in narrow bandgap photodetectors in comparison to devices employing wider bandgap materials that operate in the visible.

As progress is made towards overcoming challenges associated with losses due to recombination and increasing noise at progressively narrow bandgaps, the performance of organic SWIR photodetectors is rising with detection exceeding 10⁻¹¹ Jones, comparable to commercial germanium photodiodes. The organic photodetectors are easily integrated within a wide range of portable systems spanning wearable physiological monitors to SWIR spectroscopic imagers that enable compositional analysis for food, water quality monitoring, and medical and biological studies. There are exciting opportunities for low-cost organic SWIR technologies to be as widely deployable and serve as an empowering tool for users to discover information in the SWIR to inspire new use cases and applications.

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**8:30 AM EP04.12.02**

**Mechanically Tunable Nonlinear Dielectrics**

Deng Li Ko¹, Jie Jiang², Yu-Hong Lai¹, Pu-Wei Wu¹ and Ying-Hao Chu¹;¹Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; ²Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Hunan, China.

In the past decade, strain engineering has been used to markedly manipulate characteristics of functional materials such as increasing tunability. However, the ways to apply strain reversibly into materials such as hydrostatic pressure, strong magnetic, electric and lattice mismatch are difficult to achieve in general environment and our daily life. In this study, in order to surmount this obstacle, we adopt flexible muscovite mica substrate to fabricate epitaxial (Ba₀.₅Sr₀.₅) TiO (BSTO) thin films with high and tunable dielectric constant via van der Waals epitaxy. The combination of X-ray diffraction and high-resolution transmission electron microscopy was conducted to reveal the heteroepitaxy of the BSTO/muscovite system. Due to the mechanical flexibility of muscovite sheet, the tunability of dielectric constant were highlighted by the capacitance-voltage measurement under various bending measurement which is ranging from 5–15 mm radius of curvature including tensile and compressive strain. In the bending measurement, the dielectric constant of BSTO thin films with different thicknesses was altered nonlinearly and reversibly from -77 % to 36 % compared to the unbent state. Such a system composed of flexible BSTO/muscovite heteroepitaxy delivers a new path way to apply mechanical strain on thin film system with tunable dielectric feature.

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**8:45 AM EP04.12.03**

**From Chemistry to Mechanically-Adaptive Assemblies—Designs for Soft Thin-Film Electronics**

Stephanie Lacour and Jennifer MacRoy; Campus Biotech LSB1, Ecole Polytechnique Federale de Lausanne, Geneva, Switzerland.

Softness describes the ability of being easily shaped, conformal or folded. Stiff electronic materials may be engineered in thin, sub-micron thick, structures with 3D geometries to form electronic circuits with new form factors and reversible deformability. To increase further the circuits’ softness, a new class of materials, namely hydrogels, is emerging as a soft carrier for electronic devices. The versatility of hydrogel chemistry combined with their biomimetic properties inspires numerous applications in soft robotics, wearable and implantable electronics. However, their long-term integration within a functional electronic thin film assembly remains a challenge. In air, hydrogels dry progressively, leading to massive shrinkage of the organic network. Kept in water, they can swell up to more than ten times their initial volume thereby resulting in important mechanical stress at the interface with the electronic structure. In both cases, this significant volume change is not compatible with the cohesion of a multilayer system and has irreversible impact on the electronic properties.

This talk will report on our recent efforts to mitigate this mechanical and structural mismatch. We integrate a low-swelling type of hydrogel, the poly(2-hydroxyethyl methacrylate) [PHEMA] with thin-film electronics on polymer substrate. Because of a good balance between its hydrophilic and hydrophobic properties, we imagined a hydrogel-elastomer micrometric bilayer with a stable interface that can sustain multiple swelling-drying cycles. We will discuss the dynamic modifications of the mechanical properties of the bilayer from its initial dry state (stiff mechanical properties) to its soft and swollen state at equilibrium in wet environment. Combined with thin-film electronics technologies, this mechanically-adaptive hydrogel-elastomer assembly offers an exciting avenue for soft electronic circuits and neural devices.

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**9:15 AM EP04.12.04**

**Acoustic Assembly of Electrically Conductive Particle Structures in Flexible Printable Composites**

Drew S. Melcher¹, Tyler Ray¹, Rachel R. Collino¹, Leanne Friedrich¹, Neil Dolinski¹, Matthew Begley¹ and Daniel S. Gianola¹;¹University of California, Santa Barbara, Santa Barbara, California, United States; ²Northwestern University, Evanston, Illinois, United States; ³Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Developments in 3D-printing of flexible and integrated electronic interconnects will enable advances in the design of soft robots and other emerging flexible electronics technologies. Printing flexible interconnects with high conductivity (>10⁵ S/m) faces challenges like post-process sintering steps, resolution limitations, viscosity requirements, and substrate incompatibility that limit production speed, scalability, and cost-effectiveness. One way to overcome these challenges is to print architected composite materials with microstructures engineered for high electrical conductivity at low particle loading. We demonstrate a novel approach to accomplishing this by employing a structure-assembly technique called acoustic focusing, in which microparticles suspended in a fluid are manipulated with pressure fields generated within a microfluidic printing channel coupled to piezoelectric actuators. This technique produces composites with embedded structures that have high electrical conductivity at low particle loading in the ink (as low as 0.5% by volume). These composites are 3D-printable, have good strain tolerance, and can be modulated on-the-fly during printing to have either anisotropic conductive, nearly-isotropic conductive, or insulating behavior.

Electrically conductive filler particles (here, carbon fibers and silver-coated fibers) are aligned and compacted into dense bundles 10-200 μm in diameter, which serve as electrically conductive networks integrated within the host material. Assembly control parameters (i.e. focusing driving frequency and amplitude) and ink properties (filler fiber length and volume fraction) are modulated to adjust the composite microstructure, and thereby material properties. We demonstrate that we can form composites with anisotropic electrical conductivity (on the order of 10⁵ S/m in the printing direction within assembled bundles which are insulated from each other in the perpendicular directions), nearly-isotropic conductivity, or fully insulating behavior all using the same precursor ink. Furthermore, assembly control parameters can be modulated mid-print, so that one can switch between printing anisotropic conductive, isotropic conductive, and insulating material within the same printed line of material.

Microstructural characterization of the resulting composites reveals that the anisotropic conductive composites consist of “wires” of compacted particles insulated from each other within the material, enabling each structure to be individually addressed. These materials have sufficient conductivity to carry currents of >100 mA without heat accumulation. Furthermore, we assemble these networks in elastomeric photopolymers to form flexible conductive composites that can withstand deformation to bending strains of >20% with...
9:30 AM EP04.12.05
High-Performance Stretchable Conductive Adhesives for Bio-Compatible Stretchable Electronics Youngpyo Ko1,2, Miju Jung1, Kyung Tae Park1, Jinwoo Oh1, Soo Jin Kim1, Jung Ah Lim1, Sang-Soo Lee1,2, Wansoo Huh1 and Heesuk Kim1; 1Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul, Korea (the Republic of); 3Soongsil University, Seoul, Korea (the Republic of).

Stretchable conductive adhesives are one of the key elements in medical and wearable devices. Most interconnections of components in electronic devices have been made using Sn/Pb based solders or epoxy-based conductive adhesives. However, Sn/Pb based solders and epoxy-based conductive adhesives are not flexible and stretchable, thus leading to limitation their uses in various flexible and stretchable devices. Herein, we have demonstrated the silicone based conductive adhesive (SCA) that exhibits remarkably low resistivity of 1.5×10−4Ω cm. It maintains the electrical resistivity even when it is stretched by 2.2-fold increase in length. In addition, it shows the resistivity change of less than 3% after 3000 stretching cycles. The SCA shows excellent adhesion to various substrates such as polydimethylsiloxane (PDMS), thus enabling it to be used on various stretchable electronic devices. In order to demonstrate its versatility, the SCA has been applied to LED device as a stretchable interconnection material and electrode. Furthermore, the SCA has been used as an electrocardiogram electrode. These results indicate that the SCA with excellent adhesion to various substrates has great potential as stretchable interconnection materials and electrodes in stretchable and wearable electronics.

9:45 AM EP04.12.06
Flexible Conjugation-Break Spacers for Intrinsically Stretchable Polymer Semiconductors Jaewan Mun and Zhenan Bao; Stanford University, Stanford, California, United States.

Since the first discovery of semiconducting organic materials, tremendous effort has been made to improve their electrical properties. Their mobility exceeds that of amorphous silicon (>1 cm2 V−1 s−1), which makes them potential alternatives to inorganic electronic materials. Thanks to this significant improvement of electrical properties, research interest has now moved from mobility-oriented study to low-cost soft electronics. Along with the need for stretchable semiconductors for soft electronics, the development of intrinsically stretchable polymer semiconductors has gained much interest. However, the brittleness of conjugated polymers is a direct result of their semi-crystalline nature and rigid backbone structure. Furthermore, electrical performance and mechanical compliance of semiconducting polymers are usually inversely correlated. Thus, it is both important and challenging to develop stretchable semiconductors without sacrificing mobility. This presentation will focus specifically on using flexible conjugation breakers for stretchable polymer semiconductors. Non-conjugated spacers have been mainly utilized to enhance the solution processability of polymer semiconductors.[1-3] Reduced backbone rigidity arising from conjugation breakers can improve solution processability of semiconducting polymers. Several studies reported that these conjugation breakers can also tune mechanical properties of polymeric semiconductors.[2-3] Specifically, some non-conjugated spacers resulted in the improvement of ductility of semiconducting polymers; however, they accompanied significant compromise of electrical performance. Herein, we investigate the effect of flexible non-conjugated spacers on electrical and mechanical of semiconducting polymers.[4] Various conjugation breakers with different flexibility are synthesized and incorporated into diketopyrrolopyrrole (DPP)-based semiconductors. We show that more flexible spacers resulted in greater stretchability of semiconducting polymers without any noticeable decrease in mobility. Specifically, a dodecyl spacer exhibits both high crack onset strain of 100% and high mobility of >1.00 cm2 V−1 s−1. Furthermore, the polymer semiconductor containing the dodecyl spacer maintained much higher level of mobility than the fully conjugated counterpart under strain. Finally, fully stretchable transistors are demonstrated as a potential application of stretchable semiconducting polymers for wearable electronics. Such results show great potential for exploring conjugation-break spacers as a method of optimizing the performance of polymer semiconductors for soft electronics.


10:00 AM BREAK

SESSION EP04.13: Soft Electronics—Manufacturing and Design I

Friday Morning, April 26, 2019
PCC North, 200 Level, Room 222 A

10:30 AM EP04.13.01
Controlled Component Positioning in 3D Thermofomed Electronics Andrés Vásquez Quintero, Herbert De Smet and Jan Vanfleteren; CMST, imec Ghent University, Gent-Zwijnaarde, Belgium.

There is a growing interest in integration of sensors and electronic circuits on irregularly shaped surfaces. These 2.5D circuits can be dynamically deformable (e.g. elastic) and adopt many shapes when no other forces than gravity act on it. They can also take a predetermined fixed shape without the action of external forces. In the latter case they can either still be deformable under external forces (e.g. a smart soft lens or shoe insole) or they can be rigid and non-deformable under moderate external forces (e.g. a car dashboard with integrated electronics). In any case, for the fixed shape circuits it is desirable that the production process allows for a precise control of the components positions on the 2.5D circuit surface. In order to achieve this, the circuit can be produced on a pre-shaped 3D carrier followed by assembly of the components on the 3D circuit. This approach is e.g. used in the 3D-MID technology. However, production of circuits and assembly of components on 3D carriers is time consuming, expensive and non-standard in industrial circuit production, where all processing steps, even for flexible circuits, are carried out on flat 2D substrates. In order to comply with these standard production technology the only way is to produce the circuit on a 2D flat carrier and as a final step deform it (e.g. by a thermofoming step) from flat to its final 2.5D shape. In this case, methods should be found to precisely predict and control the component position on the 2.5D surface, starting from their positions on the 2D surface, and taking into account the effects of different parameters in the thermofoming process. In this contribution, we will describe our approach to fabricate 3D thermofomed circuits and ways to control component positions. We have found that structuring the thermoplastic polymer in which the circuit is embedded before thermofoming, provides possibilities for this components position control. We have demonstrated this approach in smart lens applications where a thin-film circuit with assembled components (chip, antenna) is deformed from flat to a spherical shape.

11:00 AM EP04.13.02
Soft Electronic and Energy Devices Based-On Laser-Induced Porous Graphene Zheng Yan; Biomedical, Biological & Chemical Engineering, University of Missouri, Columbia, Missouri, United States.

Recent research reveals that transient CO2 laser heating can convert various polymer films into porous graphene (LIG) with continuous structures under ambient atmospheres. The process is rapid and automatic, and the motorized laser beam can write the computer-designed layouts of porous graphene on polymer substrates with precisely controlled patterns. Moreover, LIG has low sheet resistance (~ 10 Ohm per square) and large surface areas (~ 150 m2/g), which is therefore a promising conducting material for a broad range of electronic and energy devices. In this talk, I will introduce our recent research in exploring soft electronic and energy devices with unusual attributes using laser-induced porous graphene. First, we have successfully made porous, multifunctional on-skin sensors, consisting of LIG as device components and PDMS sponges as substrates. The device examples include electrophysiological sensors, hydration sensors, temperature sensors, and joule-heating elements. The porous geometries of the devices could facilitate perspiration transport and evaporation, and minimize discomfort and inflammation risks, thereby improving their long-term feasibility. Second, we have achieved the construction of various 3D hierarchical structures of LIG using mechanically-guided, 3D assembly approach. The well-designed, 3D hierarchical structures of LIG exhibit outstanding electromechanical properties. Mechanical loading, such as bending, stretching and compressing, has negligible effects on their electrical performances. The device examples
include highly-stretchable LED arrays and 3D supercapacitors with solid-state electrolytes.

11:15 AM EP04.13.03
Driving Crystallization on the Way to Polymer-Based, Heterogeneous Semiconducting and Electroactive Materials
Adam Kiersnowski1, Dorota Chlebosa2 and Krzysztof Janus2
1 Wroclaw University of Science and Technology, Wroclaw, Poland; 2 Mechanics and Composite Materials, Leibniz Institute for Polymer Research, Dresden, Germany

Most ionic conductors, such as polymer electrolytes, hydrogels and ionogels, are fully transparent over visible spectrum, intrinsically deformable and biocompatible. Such transmitters or modulate electron's behavior through electrical double layer (EDL), leading to novel functions which are impossible to realize within solid-state electronics.

Electroactive and semiconducting polymer materials attract attention because of their potential applications in e.g. sensors, actuators or energy harvesting, which are crucial in development of the wearable electronic devices. In order to take advantage of such materials it is necessary to control the charge generation and charge carrier transport through their volume. The crystal phases play key roles here: crystallinity and crystal sizes as well as polymorphism and crystal orientation have crucial influence on electric properties of electronic devices. Control over the materials performance can be achieved by controlling crystallization from the length scales characteristic of crystal unit cells up to microdomain morphology.1,2

In this work we showcase the crystallization in hybrid blends based on two semicyrstalline polymers: poly(3-hexylthiophene) (P3HT): the p-type semiconductor, and poly(vinylidene fluoride) (PVDF) with remarkable piezo- and ferroelectricity. Despite dissimilar in terms of the architecture of their main chains, these polymers have an important thing in common: crystallinity-driven electrical properties. Typically, PVDF and P3HT are used in the form of films or fibers being active parts of the devices. Polymorphism and orientation of crystals in such films can be controlled during their fabrication. In the case of the solution-based processing of pure polymers, the crystallinity can be controlled by tuning polymer-solvent interactions, aggregation of macromolecules in solution, and solvent evaporation rate.2 In the case of melt-processing, the crystallinity depends mainly on the cooling regime whereas the orientation of crystals is controlled by machine-induced shearing forces or mechanical deformation after the processing.3

Blending of either PVDF or P3HT with other materials typically leads to heterogeneous systems, where the crystallinity is additionally driven by interfacial phenomena like heterogeneous nucleation or epitaxy. These together with the aforementioned effects are particularly important in nucleating the preferred polymorphs. In PVDF the ferro- or piezoelectricity are observed only for polar crystal polymorphs, i.e. the crystal forms where the unit cells are non-centrosymmetric, as in the case of Form I or Form III resulting from e.g. nucleation by e.g. silver nanoparticles. In addition, nanoparticles with high aspect ratios such as nanoplatelets of organoclay have an ability to “direct” the diffusion of the polymer chains towards the crystal growth zones, which allows formation of the oriented PVDF crystals.4 Formation of the oriented crystals of P3HT can also be driven by anisotropic nanoparticles, such as needle-like nanocrystals of perylene diimides or graphene nanoribbons.5 In the case of P3HT, however, the formation of oriented crystals results from the specific interactions between the nanofibers and the polymer.6

The orientation of the polymer crystals can be further enhanced by thermally stimulated diffusion of polymer macromolecules to the crystal growth zones, which can be achieved by e.g. local laser heating. For this purpose we have developed Laser-Assisted Zone Crystallization technique (LAZEC) enabling solution crystallization of the polymers and other organic materials under controlled thermal conditions. Application of the LAZEC in crystallization of the blends with finely tuned composition enables a large-scale formation of continuous films with controlled polymorphism and spatial orientation of polymer crystals.

The work was supported by National Sci. Centre Poland (NCN) through the grants UMO-2016/22/E/ST5/00472 and UMO-2017/25/B/ST5/02869

References:
1) Zhang G. et al; Energy & Environmental Science 11, 2018, 2046
2) Zhao K. et al; ACS Applied Materials & Interfaces 8, 2016, 19649
3) Martin J. et al; Materials Horizons 4, 2017, 408
4) Kiersnowski A. et al; Langmuir, accept. 2018
5) ElGhamel Y. et al; Nanoscale 6, 2014, 6301
6) Chlebosa D. et al; Dyes and Pigments 140, 2017, 491

11:30 AM EP04.13.04
Inkjet-Printed Iontronics Based Conformable Transparent Touch Sensors for Human Machine Interface
Dace Gao1, Jiangxin Wang1, Kaixuan Ai1, Jiaqing Xiong1, Meng-fang Lin2,3 and Pooi See Lee2; 1School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore; 2Enhanced Composites and Structures Centre, Cranfield University, Cranfield, United Kingdom

Iontronics is an interdisciplinary research topic which bridges ionics and electronics. In a hybrid iontronic system, the spatial and temporal distribution of ion species can either transmit signal or modulate electron's behavior through electrical double layer (EDL), leading to novel functions which are impossible to realize within solid-state electronics. Most ionic conductors, such as polymer electrolytes, hydrogels and ionogels, are fully transparent over visible spectrum, intrinsically deformable and biocompatible. Such remarkable optical and mechanical properties make them promising to serve as soft electrodes in applications where extreme optical transmittance or biological compatibility is stringently required. The strategy of incorporating ion conductive materials into electronic systems has enabled diverse iontronic devices spanning from artificial muscles, wearable sensors, energy harvesters, luminescent light emitters to biologically matched interfaces.

Emerging touch panels integrated in next generation wearable devices require the electrode material to be both skin-conformable and highly transparent, yet fatigue failure and sharp resistance increase are bottlenecks in stretchable and transparent electronic conductors. In this work, we demonstrated an inkjet printing-assisted iontronic touch panel with epidermal conformability and over 95% device-level light transmittance. Ionic electrolyte was directly “written” onto elastomer substrates as column and row electrodes to form a continuous films with controlled polymorphism and spatial orientation of polymer crystals.

Turning of the polymer crystals can be further enhanced by thermally stimulated diffusion of polymer macromolecules to the crystal growth zones, which can be achieved by e.g. local laser heating. For this purpose we have developed Laser-Assisted Zone Crystallization technique (LAZEC) enabling solution crystallization of the polymers and other organic materials under controlled thermal conditions. Application of the LAZEC in crystallization of the blends with finely tuned composition enables a large-scale formation of continuous films with controlled polymorphism and spatial orientation of polymer crystals.

The work was supported by National Sci. Centre Poland (NCN) through the grants UMO-2016/22/E/ST5/00472 and UMO-2017/25/B/ST5/02869

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1) Zhang G. et al; Energy & Environmental Science 11, 2018, 2046
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5) ElGhamel Y. et al; Nanoscale 6, 2014, 6301
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11:45 AM EP04.13.05
Determining the Thermomechanical Properties of Polymer Semiconductors Supported on Elastomers
Runqiao Song1, Harry Schrick2, Nrup Balar, Salma Siddika and Brendan T. O’Connor; 1 Mechanical & Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, United States

Polymer semiconductors are promising materials for stretchable electronics owing to the opportunity to tune mechanical behavior. For stretchable applications, the mechanical loading on these films is quite demanding, yet many important mechanical properties of these films related to their ability to operate over large strains has not been characterized in detail. This is due in part to the challenge of materials formulation, when forming ultrathin films, and the difficulty in measuring the mechanical properties of these films. While a large number of tools have been developed to probe ultrathin films, they all have limitations that inhibit a complete view of the film behavior. For example, the mechanical behavior of films under in-plane compression has not been captured well, which is a key part of a stretchable device that undergoes large cyclic strain. In this work, we demonstrated a novel mechanical testing technique is employed that is able to measure a broad array of mechanical properties of polymer thin films that include incompressive properties. The proposed approach consists of a polymer thin film laminated on a thin elastomer support that is then mounted in a dynamic mechanical analyzer (DMA). The elastomer provides support for the semiconductor film, but is thin enough that the properties of the polymer of interest are accurately captured. The elastomer support also provides a restoring force under large strain so that the film’s properties under compression can be obtained. By using a conventional DMA, variation in the load frequency, strain rate, and environment temperature can be used to extract detailed thermomechanical properties. In this presentation, we show the array of properties that this method can obtain from stress-strain curves under cyclic loading, to glass transitions, to stress relaxation master curves. Through this testing method, new insights into film behavior that lead to effective stretchable polymer semiconductors will be highlighted.
This presentation will describe our research efforts in developing materials for flexible and intrinsically stretchable electronic devices. A polymer composite comprising surface-embedded silver nanowires with high transparency, high surface conductivity, and low surface roughness is explored as a transparent electrode essential to the fabrication of deformable LEDs. Several electroluminescent materials are employed, including OLED, LEC, perovskite-polymer nanoocomposites.

High degrees of mechanical deformability in organic electronics (i.e., stretchability) have enabled a range of applications in energy and healthcare. These applications include large-area organic solar cells (via roll-to-roll solution printing), and wearable and implantable sensors (to allow intimate contact with biological tissues). But, polymers which have a high electronic performance and are mechanically compliant, biosafe, and easily processable remain difficult to obtain. Typically, the highest performing organic electronics are hard and undergo brittle fracture at low strains. Some of the strategies that have been reported to enhance the stretchability of conducting and semiconducting polymers include composites, blending with plasticizers, deposition on elastomers, formation of fibers and gels, and side chain engineering. While effective, each of these methods can have drawbacks in terms of biocompatibility, toxicity, ease of processing in solution, and electronic sensitivity to strain. Instead, we have investigated the use of block copolymers to obtain stretchable organic electronics. First, we reported the use of water-soluble poly(styrene sulfonate) block copolymers with poly(polyethylene glycol methyl ether acrylate) (PSS-b-PPEGMEA) as a scaffold for the conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT). The resulting conducting polyelectrolyte PEDOT:PSS-b-PPEGMEA has a toughness up to 10.1 MJ m⁻³ and can withstand elongations up to 128%. Second, we developed stretchable and degradable semiconducting block copolymers. By combining blocks of semiconducting diketopyrrolopyrrole (DPP) with insulating and flexible aliphatic poly(ethylene glycol) (PEG) blocks, we obtained materials that can be stretched >100%. Remarkably, the field-effect mobility of these block copolymers remains the same as the pure semiconductor.

In this talk, I will describe a new form of electronics with skin-like softness and stretchability, which is built upon a new class of intrinsically stretchable polymer materials and a new set of fabrication technology. As the core material basis, intrinsically stretchable polymer semiconductors have been developed through the physical engineering of polymer chain dynamics and crystallization based on the nanofluctuation effect. This fundamentally-new and universally-applicable methodology enables conjugated polymers to possess both high electrical-performance and extraordinary stretchability.[1] Then, proceeding towards building electronics with this new class of polymer materials, the first polymer-applicable fabrication platform has been designed for large-scale intrinsically stretchable transistor arrays.[2] As a whole, these renovations in the material basis and technology foundation have led to the realization of circuit-level functionalities for the processing of biological signals, with unprecedented mechanical deformability and skin conformability. Equipping electronics with human-compatible form-factors has opened a new paradigm for wearable and implantable bio-electronic tools for biological studies, personal healthcare, medical diagnosis and therapeutics.[3]

References

Upon designing high performance polymer semiconductors, degree of polymerization or molecular weight is an important polymer property that greatly affect the resulting polymer physical properties. The polymer chain length can directly influence on the morphology, packing and degree of crystallinity based on the polymer conformation and the dominating thermodynamics driving force (enthalpic vs entropic). The packing structures, especially p-p stacking distance, crystalline domain size and distribution have significant impact on not only charge transport but also thin film mechanical properties, such as modulus, ductility and deformability. Until now, it is very difficult to realize a fully conjugated rigid backbone with significant repeat units for study of the relationship between electronic performance, mechanical endurance, and molecular weight in the research community. Here we present the successful synthesis of diketopyrrolopyrrole (DPP)-based semiconducting polymers with controllable molecular weight over a wide range from approximately 20 to 100 kDa, realizing both high molecular weight and high solubility at the same time. The effects of strain on polymer thin film microstructures (alignment of polymer chains, change in crystalline domain size, degree of crystallinity and orientation), moreover, is investigated and a charge carrier mobility over up to 2 cm²V⁻¹s⁻¹ is achieved. Thanks to the relatively high molecular weight in our new polymer system, large-area biaxially stretched polymer thin film is firstly developed with superior electrical performance in stretchable devices.
Soft, noninvasive and multifunctional epidermal electronics (a.k.a. electronic tattoos or e-tattoos) have demonstrated many applications in mobile health, athletic training, human-machine interaction (HMI) and so on. However, e-tattoos are only practically useful when they are low cost and wireless. Previously, our group has invented a dry and digital manufacturing approach called the “cut-and-paste” method for the rapid prototyping of e-tattoo sensors using a paper/vinyl cutter plotter. The cut-and-pasted e-tattoos are low-cost and can be used to measure a variety of physiological signals such as electrocardiogram (ECG), skin hydration, skin temperature and so on. To make the e-tattoos go wireless, we now report the “cut-solder-paste” process to incorporate integrated circuits (ICs) such as chips for near field communication (NFC) or Bluetooth Low Energy (BLE). The key is to come up with a temporary adhesive that can survive solder-reflow temperature up to 240 degree C. To overcome the limited patterning resolution of mechanical cutter plotters and to recycle the IC chips, we propose a modular concept in which the communication layer, the readout circuit layer, and the sensor/electrode layer are fabricated individually and stacked up as the final step of fabrication. The thickness of a fully assembled multilayer e-tattoo (excluding IC chips) is less than 200 um and the overall stretchability is still beyond 20%. In addition to already mentioned capabilities, such wireless e-tattoos can also track motion, mechano-acoustic heart signals, and oxygen saturation (SpO2). The NFC-enabled e-tattoos can be wireless charged so no battery is needed but the sampling rate is limited to 25 Hz and the wireless communication distance is limited to 5 cm. The BLE-enabled e-tattoos require on-tattoo batteries but the sampling rate can be up to 4 kHz and the wireless communication range can be up to 10 m. We demonstrate that the different layers can be disassembled and reassembled multiple times. After disassembly, the communication and readout circuit layers are reusable and can be reassembled with different sensor/electrode layers. The wireless and reconfigurable capabilities and the low-cost, rapid prototyping method together represent exciting advancement towards practically useful e-tattoos.

4:00 PM  EP04.15.02
3D Designed Sensor Systems with Complex Form Factors
Woo Soo Kim; School of Mechatronic Systems Engineering, Simon Fraser University, Surrey, British Columbia, Canada.

This talk will summarize recent research activities on 3D printed soft electronics in the Additive Manufacturing laboratory, Simon Fraser University. Design, fabrication and characterization of 3D printed soft sensor systems including ion selective electro-chemical sensors, 3D printed circuit boards for portable electro-chemical sensing applications will be discussed. 3D printing enables custom design of smart 3D form factors that enable electronics to be integrated into unique places. Different electro-chemical sensor platforms such as ion-selective field effect transistor and disposable wireless RF circuits have been developed for the portable electronic applications. It is shown that 3D design integration can significantly accelerate the hybridization with the fabrication process of conventional electronics, and merge its capability into portable sensor applications.

4:30 PM  EP04.15.03
Fiber Assembly-Based Concurrent Multimodal and Multifunctional Sensors for e-Textiles
Ashish Kapoor1, Michael McKnight2, Kony Chatterjee1, Talha Agcayazi1, Hannah Kausche2, Alper Bozkurt2 and Tushar K. Ghosh1; 1Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina, United States; 2Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Soft polymer-based sensors as an integral part of textile structures have attracted considerable scientific and commercial interest recently because of their potential use in healthcare applications, security, structural health monitoring, and other applications where flexible, conformable sensors are required. While electronic sensing functionalities can be integrated into textile structures at any one or more of the hierarchical levels of molecules, fibers, yarns, or fabrics, arguably a more practical and inconspicuous means to introduce the desired electrical characteristics is at the fiber level, using processes that are compatible to textiles. Fiber-based sensors have been developed using a variety of materials such as polyethylene glycol (PEG), Kevlar, and polydimethylsiloxane (PDMS) which are doped with conductive particles such as silver, platinum, and carbon particles. A variety of techniques such as fiber extrusion, conductive coating of fibers, and 3D printing have been used to develop these sensors. Here, we report a prototype fiber-based sensor capable of multimodal and multifunctional sensing, formed within a typical woven textile structure. This is achieved by developing bicomponent fibers with ordered electrically insulating and conducting domains, composed of PDMS composites. The multifunctional characteristics of these sensors are successfully demonstrated by measuring their response to tactile, tensile, and shear deformations, as well as by their capability to detect wetness and report biopotential response. While the unobtrusive integration of sensing capabilities offers possibilities to preserve all desirable textile qualities such as comfort, flexibility, and conformability, this scaled-up fiber-based approach demonstrates the potential for scalable and facile manufacturability of practical e-textile products using extrusion-based processing of flexible sensor systems, and can be remarkably effective in advancing the field of electronic textiles (e-textiles).
bionestistic microvascular networks within mesoscale hydrogels. Our group has also pioneered bottom-up approaches to generate tissues by the assembly of shape-controlled cell-laden microgels (i.e. tissue building blocks), that resemble functional tissue units. In this approach, microgels were fabricated and seeded with different cell types and induced to self-assemble to generate 3D tissue structures with controlled microarchitecture and cell-cell interactions.

11:00 AM EP05.01.02 Fabrication of Neurobiological Circuits Liang Guo; The Ohio State University, Columbus, Ohio, United States.

Building new capabilities for the control of biological systems using embedded controllers made of biological parts to program system-level behavior holds tremendous promise to address a wide scope of both civilian and military needs. However, to date, the creation of artificial neuronal circuits that aim to perform specific functions has been proceeding at a rather slow pace due to a number of technical challenges. In order to hack the biological intelligence for behavioral and metabolic control, this work discusses the rational paths to move this field forward. Specifically, circuit design, simulation, and fabrication need to complement with new theory development to provide rational designs with optimal performance. We embody this approach through forward-engineering of simple analogs to innate neural circuits. As a first attempt, we choose to hack the Aplysia’s gill-withdrawal reflex circuit, a well-elucidated one composed of easily identifiable large neurons, so that the technical hurdles are minimized and we can focus on revealing the engineering principles and developing the engineering capability. Specifically, we identify and harvest these big neurons and reconstruct the circuit on a microelectrode array (MEA) by precisely placing and wiring the neurons according to their innate anatomical map in a photo-patterned biomaterial scaffold. The MEA is used to program long-term sensitization into this circuit and monitor its internal states. Ultimately, the advances in fundamental understanding and capabilities resulting from this project will create new opportunities for harnessing this promise of engineered biological systems for human use. The success and extension of this platform technology can have broad impacts on the advancement of medical devices, bio-robots, and human augmentation.

11:15 AM *EP05.01.03 Engineered Disease Models with Aged Tissue Microenvironments Pinar Zorlutuna; University of Notre Dame, Notre Dame, Indiana, United States.

The fact that the most significant life-threatening diseases of our times such as Cardiovascular Diseases (CVD) or Cancer remains the number one killer for over a century suggests that, despite the advancements in science and medicine over the years, there is a huge gap in translating these scientific findings to clinical setting. One of the major reasons for this gap is pre-clinical research’s heavy dependence on young animal models despite the fact that aging is the biggest risk factor for these diseases. For example, the average age for first heart attack is 65.3 years for males and 71.8 years for females, and most breast cancers develop in a postmenopausal, aged mammary gland tissue microenvironment at age of 62. Yet, due to the logistical limitations, current pre-clinical research predominately relies on experimental animals with a human-equivalent age of less than 35 years, which does not faithfully replicate the clinically prevailing aged tissue microenvironment. With increasing appreciation of the role of the tissue microenvironment in regulating disease progression and the response to therapeutics, there is an urgent need to develop, optimize and validate a novel 3D culture systems that fully recapitulates the aged tissue microenvironment in order to reproducibly model natural disease progression.

Here we present the first human induced pluripotent stem cell (hiPSC)-derived cardiomyocyte (iCM)-based, in vitro aged myocardial tissue model as an alternative research platform. Within 4 months, iCMs go through accelerated senescence and show cellular characteristics of aging. Furthermore, the model tissues fabricated using these aged iCMs, with stiffness resembling that of aged human heart, show functional and pharmacological deterioration specific to aged myocardium. We characterized hiPSC-derived cardiomyocytes (iCMs) over a prolonged culture period and determined that maturation process reaches a limit around 55 days in culture and is followed by a functional deterioration at late stages of culture (after 100 days). We show, for the first time, an in vitro aged, human-origin cardiac tissue model that is both physiologically and pathologically relevant for studying CVD such as MI. We achieved this by incorporating iCMs at the late stages into matrices with aged human heart stiffness. We show that late iCMs at cellular level and the respective tissue models at tissue level behave similar to aged human hearts, showing age-related responses, including altered gene expression and proliferative properties, impaired functional properties and stress response, decreased sensitivity to therapeutics and lower long-term viability. Our novel tissue model with age-appropriate physiology and pathology presents a promising new platform for investigating CVD or other age-related diseases.

11:45 AM EP05.01.04 Forward Design, Fabrication and Programming of Multi-Cellular Biomachines Using Neurons and Muscles Rashid Bashir; Department of Bioengineering, Carle Illinois College of Medicine, Micro and Nanotechnology Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

The integration of living cells with 3D printed soft scaffolds can enable the realization of biomachines for soft robotics and hyper-tissue engineering. Here, we will present our group’s recent efforts towards increasing force in miniature biological robots, and efforts towards integrating neural control in these biological machines. We have developed biological locomotive systems that show millinewton forces capable of driving locomotion at speeds above 0.5 mm s⁻¹. The high force was achieved by combining a ring and strip muscle design to result tissues with increased muscle cell alignment, redesign of the scaffolds, and optimized processes for cell differentiation. We also present approaches for creating neural tissue from mouse embryonic stem cell derived motor neurons that could be created within a scaffold and then integrated with these biological robots towards neuronal control. We also study neuronal plasticity in these in-vitro networks by taking advantage of optogenetic mouse embryonic stem cells, in order to start stimulation as soon as the neural progenitor stage of differentiation. We also characterized the effects of stimulation during neural differentiation, by showing morphological changes in network formation and we were also able to show that the modulations in network function could be traced back to alterations to gene expression in response to such stimulation. Such complex cellular systems will be a major challenge for the next decade and beyond, requiring knowledge from tissue engineering, synthetic biology, micro-fabrication and nanotechnology, systems biology, and developmental biology. As these “biological machines” increase in capabilities, exhibit emergent behavior, and potentially reveal the ability for self-assembly and self-repair, questions can arise about the ethical implications of this work. These devices could have potential applications in drug delivery, power generation, and other biomimetic systems.

SESSION EP05.02: Multicellular Systems and Technologies II
Session Chairs: Rashid Bashir and Liang Guo
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 226 B

1:30 PM *EP05.02.01 Emergence of Hierarchy and Functions from Cell Clusters In Vitro Taher Safi1, 2, Orn Aydin1 and Umnia Doha1; 1University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 3Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Most biological systems evolve through multiple stages of hierarchical multiplication. Individual components at a given hierarchy interact with one another to arrive at the next hierarchy with increased complexity and functionality. For example, organs and their functions emerge through interactions and cross-talk between individual cells and extracellular matrix. The rules of interactions between living biological components at various hierarchies and spatio-temporal scales are only partially understood at best. Here, we first address the question: is there a critical distance between cells necessary for the crosstalk? We address the question by considering two cell types, fibroblasts and muscle cells (C2C12) independently. We mix fibroblasts and collagen-1 and form free-discs. We find, consistent with literature, that the discs contract due to cell-ECM-cell interactions. However, compaction initiates only when the cell density exceeds a critical threshold value. We find a similar critical density for compaction in case of C2C12 cells. We differentiate the compacted C2C12-ECM tissue to myotubes when they generate force, both static and dynamic. We then plate a cluster of stem cell derived neurons in the vicinity of the muscle strip. These neurons interact with one another and form a neural network which fires in synchronous bursts. Some of these neurons are motor neurons. They innervate the muscle tissues and stimulate them in a synchronous fashion. The approach of the motor neurons towards muscle is also guided by the interactions between them possibly mediated by
soluble factors. Thus, interactions between muscle cells led to myotubes, and interactions between neurons resulted in a neural network, each arriving at a hierarchy and functionality distinct from their individual components. Finally, cross-talk between myotubes and neural network resulted in a neuro-muscular unit with complex functionality involving both sensing and actuation. Such a unit is applied to develop a living swimmer at low Reynolds number.

2:00 PM *EP05.02.02
On-Chip Interrogation of Neural Activity in Complete Nervous Systems Jacob T. Robinson; Rice University, Houston, Texas, United States.

Observing the activity of the entire nervous system as an animal responds to chemical and physical queues could reveal the fundamental principles of sensory information processing in dynamic networks of spiking neurons. Conveniently, millimeter-sized transparent organisms like C. elegans and Hydra can be manipulated on-chip using microfluidic technologies raising the prospect of high-throughput interrogation of the entire animal brain in well controlled environmental conditions. Here we describe how electrical, optical, and chemical interrogation capabilities can be integrated into scalable microfluidic devices that allow us to investigate neural information processing at the whole-brain level in living organisms. Experiments that exploit the on-chip technologies described can help reveal how adaptive networks of neurons provide robust control of animal behavior.

2:30 PM BREAK

3:00 PM *EP05.02.03
Organ-on-a-chip—Self-Rolling 3D Biosensors for Electrical Interrogations of Engineered μtissues Anna Kalmykov1, Sahil Rastogi1, Changjin Huang2, Arif M. Abdullah3, Jacqueline Billey1, Daniel Shiwarski1, K Jimmy Hsia1, Adam Feinberg1 and Tzahi Cohen-Karni1; 1Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Nanyang Technological University, Singapore, Singapore.

Since Hodgkin and Huxley’s seminal work (1952) on the electrical activity of giant squid neurons, studies of electroactive cells and tissue have been carried out using a variety of recording techniques, including glass micropipette patch-clamp electrodes, voltage-sensitive dyes, multielectrode arrays (MEAs), and planar field-effect transistors (FETs). However, multisite, simultaneous, three-dimensional (3D), and long-term electrophysiological investigation of an engineered tissue has not been possible using these technologies. Specifically, (1) voltage/ion sensitive dyes are toxic to the cells and limited in volume (3D) measurements, (2) patch clamp technique is limited by its recording sites, (3) both patch clamp and voltage sensitive dyes are limited to few minutes to hours, thus do not allow long term electrophysiological investigation of the tissue state, (4) planar FETs and MEA use established microfabrication methods to allow multiplexed detection on a scale not possible with micropipette technology, both exhibit relatively large detection areas confined to 2D substrates that render both cellular and subcellular and 3D electrical recording immensely challenging. We report a self-rolling 3D biosensors array for multiplex, simultaneous electrical measurements from excitable tissues in 3D with subcellular spatial resolution and μsec temporal resolution. Our approach directly monitors the electrical activity of microscale tissues (μtissues, ca. 300μm) engineered from induced pluripotent stem cell (iPSC) derived cardiomyocytes.

3:30 PM EP05.02.04
Microfiber-Guided Fabrication of Accurately Wired Neural Circuits Yu Wu, Meijian Wang, Huiran Yang, Hao Qi, Benjamin Seicol, Jordan Prox and Liang Guo; The Ohio State University, Columbus, Ohio, United States.

Functional biological devices made from living cells have the advantage of much less foreign body responses than non-biological implants. To engineer such neurobiological circuits, research to date still stays on the level of random neural patterning without knowing the function of each neuron, whereas neurons are precisely wired and functionalized in intact animals. As a result, the missing recognition of both components’ functions and connections becomes a major obstacle for rational design of neurobiological circuits. Based on the finding that neurite growth can be guided by microfibers, we developed a patterning technique enabling alysia neurons to be precisely wired with each other without cross-communication. We implement a microfiber scaffold using photolithographically fabricated SU-8 microfibers combined with selective surface coating of poly-l-lysine. Our results show that axons of alysia neurons adhere to the side walls of microfibers and grow along to reach to adjacent target neurons. This simple and effective technique enables rational design and functional fabrication of neurobiological circuits as potential living neural implants.

3:45 PM *EP05.03.05
Bottom-Up Approaches for Controlling Cell Behavior—Interfacing Synthetic Biology and Biomaterials Tara L. Deans; Department of Biomedical Engineering, The University of Utah, Salt Lake City, Utah, United States.

All tissues are composed of lineage committed cells and an extracellular matrix (ECM) that is secreted and maintained by the surrounding cells. Stem cells are an important cell population for tissue maintenance, regeneration, and repair because they have the ability to replenish their own population, and to differentiate into a number of cell types to restore tissue function. Both intrinsic as well as extrinsic mechanisms have been shown to be involved with the regulation of stem cell self-renewal and differentiation, and this interplay between intrinsic and extrinsic cues has made it difficult to direct an entire population of stem cells toward a desired lineage. This talk will describe approaches for interfacing synthetic biology and materials science to engineer genetically interactive biomaterials and programmed ECMs to control intrinsic and extrinsic cellular events to control cell behavior. Altogether, these novel approaches can be used to improve cell fate outcomes, in addition to reprogramming terminally differentiated cells to function as novel therapeutic diagnostic and delivery vehicles.

SESSION EP05.03: Bacterium- and Biomolecule Based Systems and Technologies
Session Chairs: Liang Guo and Elizabeth Strychalski
Wednesday Morning, April 24, 2019
PCC North, 200 Level, Room 226 B

8:30 AM *EP05.03.01
Acoustic Biomolecules for Non-Invasive Ultrasonic Imaging and Control of Cellular Function Mikhail Shapiro; California Institute of Technology, Pasadena, California, United States.

The study of biological function in intact organisms and the development of targeted cellular therapeutics necessitate methods to image and control cellular function in vivo. Technologies such as fluorescent proteins and optogenetics serve this purpose in small specimens or surgically accessed tissues, but are limited by the poor penetration of light. In contrast, most non-invasive techniques such as ultrasound and magnetic resonance imaging – while based on energy forms that penetrate tissue effectively – are not effectively coupled to cellular function. Our work attempts to bridge this gap by engineering biomolecules with the appropriate physical properties to interact with magnetic fields and sound waves. In this talk, I will describe our recent development of biomolecular reporters and actuators for ultrasound. The reporters are based on a unique class of gas-filled protein nanostructures from buoyant photosynthetic microbes. These proteins produce nonlinear scattering of sound waves, enabling their detection with ultrasound. I will describe our recent progress in understanding the biophysical and acoustic properties of these biomolecules, engineering their mechanics and targeting at the genetic level and expressing them heterologously as acoustic reporter genes. Our actuators are based on temperature-dependent transcriptional repressors, which provide switch-like control of bacterial gene expression in response to small changes in temperature. This allows us to use focused ultrasound to remote-control engineered bacteria in vivo. Finally, I will describe how we have used ultrasound in combination with viral vectors and engineered receptors to provide spatially and cell-type specific non-invasive control over neural activity.

9:00 AM *EP05.03.02
Microfluidics Synthesis of Gene Silencing Cubosomes Hojun Kim and Cecilia Leal; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

The design of nanoscale reservoirs for efficient delivery of drugs and nucleic acids to cells is an enduring challenge in materials for medicine. Drug-loaded liposomes have enabled numerous FDA approved systems for several diseases. However, many of the applications of molecular materials are often discontinued. This is because they fail to deliver cargo
Multiple Mechanisms of Short-Term Presynaptic Plasticity Realized in Peptide-Doped Biomembranes

Joseph S. Naijen1,2, Patrick Collier1 and Stephen A. Sarles2; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2The University of Tennessee, Knoxville, Knoxville, United States.

It is through modifications of synaptic transmission (i.e., synaptic plasticity) between neurons that the brain is capable of adapting, learning, and modifying its functions in response to stimuli. Synaptic transmission can be either enhanced or depressed by brain activity, and these changes can last from milliseconds to a lifetime. They can occur in the form of short-term plasticity, which we demonstrated that insulative lipid membranes formed at the adjoining interface of lipid-coated aqueous droplets in oil exhibit memory capacitance stemming from voltage-driven modulation in the area and thickness of the hydrophobic core of the membrane. We show how introducing spontaneous, pore-forming, gramicidin peptides into the insulating lipid membrane creates conductive pathways—transforming the inherently memcapacitive device into a memristor that exhibits a pinched hysteretic current-voltage relationship. Experiments are performed to characterize the sensitivities and dynamics of membrane geometry changes and channel forming kinetics in response to voltage. Further, we developed a mathematical model that describes the physical states (membrane area, thickness, and channel kinetics) of the system involved in the memristive response. From both, we learn that the kinetics of channel formation by gramicidin peptides are extremely fast in comparison to the rates of dynamic modulations in bilayer area and thickness—suggesting that hysteresis and memory are dominated by the rates of change in membrane geometry. Our modular peptide doped bio-membrane also exhibits short-term synaptic-like facilitation and depression, emulating mechanisms of short-term plasticity exhibited by ion channels in pre- and post-synaptic neurons. Thus, our findings forecast an alternative paradigm of smart hardware using soft materials with simple composition and fabrication yet capable of providing inherent synaptic properties.
While it is clear that bacteria in the gut can impact brain function, many fundamental questions about the information processing along the brain-gut-axis remain. We developed a unique model for probing the earliest in-vivo brain-body interface, using Xenopus laevis (frog) developmental model, revealing that the nascent brain, even before being fully formed, contains and sends instructive information for morphogenesis of remote tissues. This brain-body information interchange is mediated by ancient bioelectrical mechanisms, suggesting the possibility of a well-conserved computational code that could be shared by the microbiome. Our latest results demonstrated communication between brain and pathogenic bacteria, showing that the brain is involved in regulation of innate immune response to infection. Transcriptome data indicate pathways and sub-networks involved in brain-dependent and brain-independent regulation of the infection, proposing several novel targets for top-down control of information processing across different scales of biological organization. We are thus undertaking a computational analysis of the information content of the cross-talk between bacteria and neurons in vitro. Using techniques from neuroscience, biophysics, molecular biology, synthetic bioengineering, and information theory, we are developing and fabricating the first integrated electrical-optical brain-bacteria interface (BBI), a multi-site stimulation and recording platform specifically suited to extract information in real-time across highly diverse biological entities. The BBI is a microfluidic, optogenetic, and electrophysiological platform consisting of i) a cultured vertebrate brain or brain organoid, ii) a bacterial biofilm, and iii) a closed-loop software-controlled actuation and sensing system which extracts bioelectrical measurements from the brain and the bacteria under a series of real-time perturbation and uses mutual information analysis to determine how much each side knows about what is happening to the other. Currently, we are validating the health of the two biological components (long-term co-culture of neurons and bacteria), verifying that we can read and write information into the system. We are monitoring information transfer both optically, through fluorescent genetically-encoded ion reporters, and electrically, through the design and constructing of customized micro-electrode-array on microfluidic chambers. Chemical stimuli (drug screening) are provided via microfluidics. Next steps will characterize the communication channel and generate a quantitative model of cross-level communication. Finally, we will manipulate and re-write active communication between components to test and refine specific hypotheses. The extraction of informational content from signaling between prokaryote and metazoan systems will produce exciting new knowledge of both basic and applied (biomedical) impact, bridge a capabilities gap that establishes a new direction for synthetic bioengineering, and serve as an enabling technology and proof-of-principle analysis that many other labs will be able to use to addressing major challenges from different perspectives (from cellular/biological or synthetic constructs to multicellularity and evolution).

**SYMPOSIUM EP06**

Organic Electronics—Materials and Devices
April 23 - 25, 2019

**Symposium Organizers**
Paddy K. L. Chan, University of Hong Kong
Oana Jurchescu, Wake Forest University
Joannis Kymissis, Columbia University
Brendan O'Connor, North Carolina State University

**Symposium Support**
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* Invited Paper

**SESSION EP06.01: Modeling**

Session Chairs: Paddy K. L. Chan and Joon Hak Oh
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 222 C

10:30 AM *EP06.01.01*

**Will We See Gigahertz Organic Transistors?**

Hagen Klauk; Max Planck Institute for Solid State Research, Stuttgart, Germany.

Despite all efforts to advance the performance of organic transistors, their transit frequencies remain far below 1 GHz. The reason is that previous efforts have focused mainly on parameters that have little or no impact on the high-frequency performance. By analyzing the fundamental equations for the transit frequency, the requirements for gigahertz performance are derived. Not surprisingly, the critical parameter in this quest is not the charge-carrier mobility, but the contact resistance.

11:00 AM *EP06.01.02*

**Understanding Tunnel Currents in Organic Transistors—From New Theoretical Models to New Devices**

Shiyi Liu1, Akram Al-Shadeedi2, Max Tietze2, Chang-Min Keum3 and Bjorn Lüssem1; 1Kent State University, Kent, Ohio, United States; 2Center for Surface Chemistry and Catalysis, University of Leuven, Leuven, Belgium; 3School of Physics & Astronomy, University of St Andrews, St Andrews, United Kingdom.

A thorough understanding of tunnel currents in disordered organic semiconductors is essential to understand charge transport and injection into disordered organic semiconductors1–3. Furthermore, tunnel currents provide an additional parameter space to design novel devices, e.g. organic Zener-Diodes4,5, AC-driven OLEDs6, or inversion type OFETs7–9. In this presentation, we introduce a generic model to describe HOMO to LUMO tunneling in organic Zener diodes is presented. It is shown that the particular shape of the density of states in the organic layer determines the breakdown voltage in these diodes. Furthermore, the ideality factor of the diodes is shown to be limited by the width of the density of states and the roughness of the organic layer.

Based on this model, approaches to widen the design space of organic field-effect transistors are discussed. It is shown how HOMO to LUMO tunneling can be used to facilitate ambipolar injection and generation of minority charge carriers in organic field-effect transistors. Furthermore, the design and performance of Organic Field-Effect Transistors is presented and ways to improve their performance are discussed.

Flexible FET-Type Sensors Based on Nanoscopically Engineered Organic Semiconducting Materials

Enrique D. Gomez; The Pennsylvania State University, State College, Pennsylvania, United States.

We have recently demonstrated approaches that tune the molecular structure to suppress energetic disorder at interfaces and suppress coherent lattice vibrations in small molecule semiconductors to enhance charge mobilities. We control chain conformations within high-k fluorinated polymers, minimize energetic disorder at the dielectric—semiconductor interface, and enhance charge mobilities in rubrene single-crystal devices. Copolymerization of vinylidene fluoride and bromotrifluoroethylene (VDF-BTFE) monomers yields photopatternable, high-k fluoropolymer poly(vinylidene fluoride-bromotrifluoroethylene), (PVDF-BTFE). BTFE moieties allow crosslinking through thermal- or photocuring, and crosslinking of polymer chains perturbs the chain conformations within the polymer films. Devices incorporating hot-pressed, crosslinked (P(VDF-BTFE) as the dielectric and rubrene single crystals as the active layer exhibit lower interfacial trap densities compared to SiO2 and other polymer dielectrics, as well as charge mobilities exceeding 10 cm²/Vs. These charge mobilities are more than an order of magnitude higher than mobilities of rubrene single-crystal OFETs comprising poly(vinylidene fluoride-tetrafluoroethylene) (PVDF-TrFE) copolymers as gate insulator layers, and are the highest charge mobilities reported to date for devices incorporating high-k (k > 3) polymer dielectrics. Furthermore, we show that alkyl side chains can disrupt key modes of lattice vibrations that limit transport. We explore a model series based on [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) derivatives where we systematically add one or two octyl side chains. Single crystal field-effect transistors made from these materials show an enhancement in hole mobilities by nearly three orders of magnitude upon addition of alkyl side chains in active layer materials. Quantum calculations based on the static structure cannot predict this large variation in charge mobilities. Instead, melastatic neutron scattering spectra (of deuterated BTBT derivatives) show that the addition of alkyl side chains suppresses picosecond intermolecular lattice vibrations, thereby enhancing charge mobilities in devices. Thus, although a trade-off has been hypothesized between disrupting charge transport and enhancing solubility due to the addition of alkyl side chains, we instead show that the addition of alkyl side chains can enhance charge mobilities by multiple orders of magnitude.

Organic electronics is a valuable technology for the development of novel applications in different fields, ranging from bioelectronics to smart packaging and displays. Transparency and compliance are often fundamental features for an effective device functionality and integration into complex systems. Several examples of organic devices, including diodes and Organic Field-Effect Transistors (OFETs) on transparent and ultra-flexible substrates, have been reported in literature. In the case of OFETs, however, the fulfillment of these characteristics is often related to the employment of small area, small throughput techniques which are not suited for the final development of complex applications and possibly up-scaleable for production. Moreover, low voltage operation is complex to be obtained with cost-effective, large area techniques, in particular when organic materials are employed in order to improve transparency of devices. As a matter of fact, low voltage transparent OFETs fabricated using cost-effective, large area techniques with enhanced transparency and conformability are absent in literature. Nevertheless, filling such a gap is fundamental in order to obtain fully functional systems that can be effectively employed in bioelectronics and electronics applications.

Here, an original approach for the fabrication of transparent, low voltage, all-organic FETs by means of large area techniques is presented. Two cost-effective, large-area techniques easily up-scaleable to an industrial size, namely inkjet printing and chemical vapor deposition, were employed for device fabrication. In particular, inkjet printing was used for patterning transistor electrodes using a PEDOT:PSS-based commercial ink, and for the deposition of the p-type, organic semiconductor, namely TIPS pentacene, from a custom-made solution. Chemical Vapor Deposition was used for the deposition of the organic insulator, namely Parylene C, in a uniform, 200-nm thick film allowing the low voltage operation. The overall transistor structure is perfectly transparent, as demonstrated by absorbance characterization in the range of visible light. More than 50 devices have been successfully fabricated over 175um-thick polyethylene terephtalate (PET) substrates: electrical characterization carried out before and after transferring on the skin demonstrated that the device functionality is perfectly maintained. Moreover, the ultra-thin OFETs were employed for the fabrication of basic electronics circuits, such as pseudo-CMOS inverters, which were successfully tested on skin. These results pave the way for the development of transparent organic electronics for different kind of applications, including bioelectronics and tattoo-like electronics.

Achieving Ultra-Low Turn-On Voltages in Organic Thin-Film Transistors—Investigating Fluoroalkyl-Phosphonic Acid Self-Assembled Monolayer Hybrid Gate Dielectrics

Rachana Acharya; 1 Boyu Peng; 1 Paddy K. L. Chan; 2 Guido Schnitz; 2 and Hagen Klauck 1; Max Planck Institute for Solid State Research, Stuttgart, Germany; 2 Institute of Materials Science, University of Stuttgart, Stuttgart, Germany; 1 Department of Mechanical Engineering, University of Hong Kong, Hong Kong, Hong Kong.

The optimization of organic thin-film transistors (TFTs) to address specific analog and digital circuit design requirements depends heavily on the choice of the materials employed, particularly the organic semiconductor and the gate dielectric. For a particular organic semiconductor, the performance must be reviewed with different combinations of substrate material, fabrication conditions and the choice of the gate dielectric material in order to achieve the optimum TFT characteristics for particular device and circuit needs. We have fabricated and characterized organic TFTs using the small-molecule organic semiconductor 2,7-diphenyl[1]benzothieno[3,2-b][1]-benzothiophene (DPh-BTB) [1] in combination with a hybrid gate dielectric composed of aluminum oxide and a fluoroalkyl-phosphonic acid self-assembled monolayer. We find that the optimum substrate temperature during the vacuum deposition of the DPh-BTBT layer depends on the type of substrate on which the organic TFTs are fabricated. For vacuum-deposited DPh-BTB to form a clear layer with the highest possible charge-carrier mobility, the semiconductor deposition should be carried out with the substrate held at a temperature of 100°C on silicon substrates...
and without substrate heating on flexible plastic substrates. XRD measurements indicate different orientations of the DPh-BTBT molecules under different fabrication conditions, which can be correlated to the TFT performance. Furthermore, fluoroalkyl-phosphonic acids with fluoroalkyl chain lengths ranging from 6 to 14 carbon atoms have been used to vary the thickness of the self-assembled monolayer in the gate dielectric, and its influence on the TFT characteristics has been studied. The fluoroalkyl terminal groups facilitate a shift of the TFTs turn-on voltage [2] in a deterministic manner, e.g., to exactly 0 V, if so desired from a circuit-design perspective, while taking advantage of the possibility to optimize the other TFT parameters by selecting the optimum fluoroalkyl chain length. We find that a medium fluoroalkyl chain length (10 carbon atoms in the fluoroalkyl chain) leads to the highest charge-carrier mobility (0.4 cm²/Vs on flexible plastic substrates, 1 cm²/Vs on silicon substrates) and the largest on/off current ratio (above 10⁶). [1] K. Takimiya et al., J. Am. Chem. Soc. 128, 12604, 2006. [2] U. Kraft et al., J. Mater. Chem. 20, 6416, 2010.

2:30 PM *EP06.02.04
Designing Solution-Processed Photonic Light- and Heat-Management Structures for Optoelectronic Devices
Natalie Stingelin; Georgia Institute of Technology, Atlanta, Georgia, United States.

An ever increasing interest in the development and application of innovative optical and optoelectronic devices places greater emphasis for the advancement of new smart and functional materials that are readily processable. Significant progress has already been realised in the fields of organic light-emitting diodes (OLEDs) and photovoltaic cells (OPVs) through development of novel semiconducting materials. Here we discuss developments and advancements in materials design towards photonic structures that aid and improve light management in organic and inorganic/organic hybrid devices. Here, we cover systems targeted for use in light input/output-coupling structures, anti-reflection coatings, waveguides, and beyond. Extension to architectures for heat management, important e.g. for a broad range of photovoltaic device platforms, will also be presented.

3:00 PM BREAK

3:30 PM *EP06.02.05
Large-Area Organic Single-Crystal Semicconductors for Integrated Circuits
Jun Takeya; University of Tokyo, Kashiwa, Japan.

In field-effect transistors, charge is accumulated in only a few-nanometer-thick surface of semiconductors interfacing gate-insulating layers, so structurally well-defined molecular-layer single-crystal films of organic semiconductors are highly beneficial in saving the material. We recently succeeded in growing highly homogeneous organic semiconductor films of ultrathin single crystals, so that high values of charge-carrier mobility exceeding 10 cm²/Vs is achieved everywhere in the dimensions of 10 cm x 10 cm substrates. Named as “organic single-crystal wafers” the multilayer films are ready to be fabricated to CMOS integrated circuits. P- and n-type organic semiconductor materials are newly synthesized for high-mobility carrier transport based on strategies of minimizing effective masses and phonon scattering rates. Both layers are formed by solution from continuous crystallization at the edge of coating blades. With recent development of key processing technologies for printed LSIs, low-cost platforms for RFID tags, AD converters, data processors, and sensing circuitries will be displayed. In particular, developing simple integrated devices based on CMOS using the p-type and n-type printed organic FETs, successful rectification and identification are demonstrated at 13.56 MHz with printed organic CMOS circuits.

4:00 PM EP06.02.06
Stability of Printed Organic Thin-Film Transistors Composed of Ultrafine Silver Electrodes by SuPR-NaP Technique
György Kitahara1, Takamasa Hamai2, Satoshi Matsuoka1, Shunto Arai3 and Tatsuaki Hasegawa1,2; 1The University of Tokyo, Tokyo, Japan; 2AIST, Tsukuba, Japan.

Solution-based productions of both metal and semiconductor patterned layers are the essential components for printed electronics technologies that have made considerable progress in recent years. Next important challenge is to combine and integrate the respective printing techniques, for realizing high-performance, highly-stable, and all-printed organic thin-film transistors (OTFTs). Here we demonstrate that stable operations become possible in solution-processed OTFTs, when they are composed of ultrafine silver electrodes that are produced by the “surface photo-reactive nanometal printing (SuPR-NaP)” technique [1]. The SuPR-NaP technique is based on a silver-nanoparticle chemisorption effect on photo-activated patterned perfluoropolymer surfaces, which allows easy, high-speed, and large-area manufacturing of ultrafine metal wiring. In the fabrication of bottom-gate, bottom-contact-type OTFTs, we used spin-coated layer of perfluoropolymer, Cytop (Asahi Glass Co., Ltd.), that functions as a base layer for producing patterned photo-activated surface in the SuPR-NaP technique for producing source/drain electrodes but also as a gate dielectric layer (combined with base silica/Si substrates) [2]. As the surface of Cytop layer is extremely hydrophobic, we used unique “push-coating” technique to produce uniform polymer semiconductor channel layer on the Cytop layer with source/drain electrodes [3]. For reference, we also prepared OTFTs without Cytop layer on silica/Si substrates, where source/drain electrodes were fabricated by vacuum deposition of Au. We found that the OTFTs with hydrophobic Cytop layer exhibit much higher carrier mobility (more than 10 times larger) than that of the devices without Cytop layer on silica/Si substrates. Additionally, the performance of the former devices is featured by negligible hysteresis and small threshold voltage around 0 V, where threshold voltage shift due to gate bias stress is effectively suppressed, as compared to the large hysteresis of about 3 V in the latter devices. We discuss the origin of stable and highly-efficient operations of the printed OTFTs, in terms of the elimination of carrier traps in the high-quality gate dielectric/semiconductor interface realized with Cytop in the SuPR-NaP technique [4,5].


4:15 PM EP06.02.07
Electronic, Optical and Electrical Properties of Single Crystal Dinaphtho-Thieno-Thiophene (DNTT) Sunita Pookpannang1, Emily Bittle2, Christina Hacker3, Andrei Kolmakov1, Steven Robey1, Erika Giangrisostomi1 and Ruslan Ovsyannikov2; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

Organic semiconductors can be integrated onto device structures in different physical forms such as single crystals, polycrystalline thin-films, or amorphous thin-films. There are many studies which have shown that by altering molecular orientation or packing, the extrinsic properties of an electronic device properties can be impacted. The structural order of the molecular solid profoundly influences the electronic properties, that in turn controls important properties, such as the transport gap and energetic level of the highest occupied molecular orbital (HOMO). While there are numerous photoemission spectroscopic measurements of organic semiconductors in thin-film structures, far fewer attempts have been made to determine the “fundamental” electronic properties for pristine organic single crystals. We present results of photoemission measurements for single crystalline (SC) dinaphthothieno-thiophene (DNTT). DNTT is a small molecule-based thienoacene and has demonstrated carrier mobilities approaching 10 cm²/Vs [1], is air-stable [2] and durable against accelerated temperatures and humidity conditions. Electronic “band” structure measurements using a novel angle-resolved time-of-flight electron spectrometer is performed on SC-DNTT, and multiple highest occupied molecular orbitals are resolved of varying widths. Modest dispersion of the frontier HOMO is observed. Using polarized Raman spectroscopy, the orientation of the crystal unit cell can be identified. The electronic structure results will be discussed in context of the electronic structure calculations and charge carrier behavior of DNTT reported in the literature.


4:30 PM EP06.02.08
Mimicking Associative Learning Using Synapse-Like Non-Volatile Organic Electrochemical Transistor
Xudong Ji, Gary K. K. Chik and Paddy K. L. Chan; University of Hong Kong, Hong Kong, Hong Kong.

Since the last decade, the synaptic electronics has attracted much more attention due to its computational parallelism, fault tolerance as well as energy efficiency. These excellent
Polymer Light-Emitting Diodes with an Emitting Layer Based on a Nano-Confined Semiconducting Polymer Blend

Anielen Ribeiro, Paul Blom and Jasper Michels; Max Planck Institute, Mainz, Germany.

Blending a visible light-emitting organic semiconductor with an insulator alleviates the trap-limited nature of the electron current. Organic light emitting diodes (OLEDs) comprising such a blend as emissive layer exhibit a two-fold increase in luminous efficiency with only 10% semiconductor. Due to this low content of semiconductor, polymer-LEDs are more attractive than small molecule-based devices. However, polymers impose the difficulty of an inherently low miscibility. In a plain blend macro-phase separation can be avoided if the molecular weight is kept low, which, in case of the semiconductor, is a disadvantage as it suppresses charge carrier mobility. An alternative strategy is to impose a nano-confinement. We prepare aqueous nanodispersions of red (PPV) and blue (polyfluorene) emitting polymers, blended with polystyrene as an insulator. We seem to fully suppress macro-phase separation in both cases. For the latter, the combination of nano-confinement and blending influences the phase morphology of the semiconductor in an unprecedented way. Fabricating OLEDs with an emitting layer consisting of nanoparticles poses a considerable challenge due to high operational current densities. We now succeed in fabricating such devices in a reproducible way at very decent efficiencies.

Physical and Electronic Properties of COF-5 Films with Intercalated Metal Ions

Michael S. Bible, Emma F. Dohnmeier, Lindsey R. Guthrie, Justin Hendrix, Joseph R. Hunt and Michael S. Lowry; U.S. Department of the Navy, Dahlgren, Virginia, United States.

The ability to tailor the geometric arrangement and electronic structure of materials is appealing for a broad range of applications including energy storage, micro-electronics and electromagnetic shielding. This project aims to develop and study a series of new materials to gain insight into methods for controlling the electromagnetic properties of two-dimensional covalent organic frameworks (2D-COFs). 2D-COFs are porous, semi-planar and stackable macromolecular structures, which can serve as a scaffold for additive materials to yield novel performance. The experimental work reported herein focuses on the synthesis of a 2D-COF and the development of methods for incorporating ionic compounds and examining resultant changes in electronic structure. In-situ and ex-situ methods of intercalation have been explored/optimized, and advanced structural and property characterization techniques have been employed on these new materials. Preliminary findings have already shown induced changes in the physical and electronic properties of perhaps the most common 2D-COF. The results of these studies show promising trends that will be expanded upon by future investigations.

Influence of Trapping Effects on Organic Memory Devices

Ulli von Goscinski, Kavita Singh Ghotra, Maxim Kempf and Klaus Meerholz; Chemistry, University of Cologne, Cologne, Germany.

The ability to tailor the geometric arrangement and electronic structure of materials is appealing for a broad range of applications including energy storage, micro-electronics and electromagnetic shielding. This project aims to develop and study a series of new materials to gain insight into methods for controlling the electromagnetic properties of two-dimensional covalent organic frameworks (2D-COFs). 2D-COFs are porous, semi-planar and stackable macromolecular structures, which can serve as a scaffold for additive materials to yield novel performance. The experimental work reported herein focuses on the synthesis of a 2D-COF and the development of methods for incorporating ionic compounds and examining resultant changes in electronic structure. In-situ and ex-situ methods of intercalation have been explored/optimized, and advanced structural and property characterization techniques have been employed on these new materials. Preliminary findings have already shown induced changes in the physical and electronic properties of perhaps the most common 2D-COF. The results of these studies show promising trends that will be expanded upon by future investigations.
Organic memory devices (OMEs) are realized by integrating a layer of the crosslinkable dithienylethene XDTE in a solution-based multilayer OLED stack. The photochromic XDTE molecule can be switched reversibly by a photo- and/or electrically induced ring-opening/-closing reaction to two thermally stable states featuring different physical properties. The change in the energy level positions, which is responsible for controlling the hole injection by shifting the hole injection barrier, enables a high ON/OFF ratio approaching 10^4. For future application as data storage element, electrically induced switching is of great importance, but the charge trapping landscape is affected by this switching mechanism. By incremental switching via current densities pulses, intermediate switching states are accessible. The current-response is analysed as a function of the fraction of closed isomers obtained via in-situ reflectance absorption spectroscopy. In combination with impedance spectroscopy measurements, we study the role of trapping effects in this energetically anisiotropic switching process.

EP06.03.04 All-Room-Temperature Solution-Processed New Noncopolymers Based Hole Transport Layer from Synthesis to Film Formation for High-Performance Organic Solar Cells Towards Ultimate Energy-Efficient Fabrication Zhanheng Huang1, Jiaqi Chen1, Xingang Ren1, Jiaqi Zhang1, Vellaayassis A. Roy1, Jeffrey M. Burkhartmeyer2, Kam S. Wong2 and Wallace C. Choy; 1The University of Hong Kong, Hong Kong, Hong Kong; 2Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, Hong Kong; 3City University of Hong Kong, Hong Kong, Hong Kong.

The ultimate goal of energy-efficient fabrication of photovoltaic devices requires low energy consumption processes covering both synthesis of material and fabrication of device. Regarding to charge transport layer, it is worthwhile to synthesize nanomaterials and deposit films all at room temperature while still have good electrical properties. In our work, we propose and demonstrate a new nanocomposites of maghemite and iron hydroxide through a low energy consumption approach which is all room-temperature solution process of the syntheses from the nanocomposites to the formation of high quality hole transport layer (HTL). Strategically adjustment of acidity for the conversion of prepared precipitation is demonstrated to achieve a component controllable maghemite and iron hydroxide nanocomposites which contributes to in-situ tunable work function of the nanocomposites HTL from 4.70 eV to 5.16 eV. Simultaneously, since the nanocomposites synthesized in this approach has the features of ultra-small size of 6–10nm and surfactant-free, high quality and efficient HTL films can be formed at room temperature. For organic solar cells using nanocomposite as HTL, the power conversion efficiency can be significantly improved by as much as 80% compared with the optimized devices without HTL. Besides, both the efficiency and stability of the nanocomposite based organic solar cells are better than that of devices using poly (3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS). Consequently, the work contributes to the fabrication of simple, low-cost, and stable optoelectronics promoting green photovoltaics and flexible electronics.

EP06.03.05 Dual-Conformation Fluorescent Emitters—From Stimuli-Responsive Materials to Highly Efficient Organic Light-Emitting Diodes Shi-Jian Su; South China University of Technology, Guangzhou, China.

One typical strategy for designing fluorescent emitters is to combine an electron donor (D) unit and an electron acceptor (A) unit via a π conjugation link. A large spatial separation of the frontier orbitals can be achieved by a large twisting angle between the D and A units to give a small singlet-triplet splitting energy (ΔE_{ST}) and thus thermally activated delayed fluorescence (TADE). On the contrary, a small twisting angle will generally enlarge the HOMO-LUMO orbital overlap due to a weak intramolecular charge transfer (ICT) to give a conventional fluorescence emitter. We found that some D-A molecules have dual conformations and thus dual fluorescence emissions, where one emission involves weak ICT excited states and the other comes from strong ICT excited states with a large Stokes shift. Such dual fluorescence emissions can be exploited for stimuli-responsive fluorescence materials, achieving white-light emission combining blue conventional fluorescence and yellow TADF from a single compound in various states due to controllable conformational distribution. In addition, dual fluorescence emissions can also be suppressed by improving molecular rigidity to give TADF-dominated emission with efficient reversed intersystem crossing from triplet state to singlet state. Corresponding organic light-emitting diodes (OLEDs) also achieved high efficiencies and reduced efficiency roll-off.

EP06.03.06 Utilization of Divinyl Sulfone as a TADF Acceptor Core Joshua T. Keubeck1, Allison Lim2 and Alan Sellienger1, 2, 3; 1Chemistry, Colorado School of Mines, Golden, Colorado, United States; 2Material Science Program, Colorado School of Mines, Golden, Colorado, United States; 3National Renewable Energy Laboratory, Golden, Colorado, United States.

A comparative study of thermally activated delayed fluorescence (TADF) properties of sulfone analogues are reported. Synthesis of multiple divinyl sulfones (DVSs) and their sulfone analogues have been explored via computational and experimental methods to determine the effects on the TADF properties. Utilization of DVS as the acceptor imparts several beneficial properties to the emitters: 1) increased separation between the donor and acceptor groups; 2) enhanced separation of the frontier orbitals; and 3) decrease in crystallinity. These properties lead to a smaller single-triplet energy gap thereby potentially improving TADF emission, and film imperfections caused by crystallization. Synthesis of selected compounds have been achieved via palladium catalyzed couplings followed by nucleophilic aromatic substitution using aromatic amine donors. Air versus argon solution photoluminescence, solution photoluminescent quantum yield, single-triplet state energy gap, density functional theory, thermal properties, and initial OLED results will be presented.

EP06.03.07 Work Function Modification of Indium-Tin Oxide by a Combination of Charge-Based Through-Space Interaction and Surface Interaction Da Soel Yum1, David Bilby1, Kyeongwoon Chung1, Jill K. Wendorf1, 2, Jacob Jordahl1, Bo Hyun Kim1, Joerg Lahnn1, Peter F. Green1 and Jinsang Kim1; 1University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Northwestern University, Evanston, Illinois, United States; 3Korea Institute of Industrial Technology, Cheonan, Korea (the Republic of); 4National Renewable Energy Laboratory, Golden, Colorado, United States.

Organic electronic devices rely upon the work function of their electrodes for control over charge injection and built in electric fields. However, an explanation of the origin of work function modification remains unclear. With a representative polyelectrolyte set, we studied how the work function of electrodes can be modified by a combination of charge-based through-space interaction and surface interaction. The formation of a surface dipole due to a through-space interaction between the modifying layer and substrate can be achieved by a large twisting angle between the D and A units to give a small singlet-triplet splitting energy (ΔE_{ST}) and thus thermally activated delayed fluorescence (TADE). On the contrary, a small twisting angle will generally enlarge the HOMO-LUMO orbital overlap due to a weak intramolecular charge transfer (ICT) to give a conventional fluorescence emitter. We found that some D-A molecules have dual conformations and thus dual fluorescence emissions, where one emission involves weak ICT excited states and the other comes from strong ICT excited states with a large Stokes shift. Such dual fluorescence emissions can be exploited for stimuli-responsive fluorescence materials, achieving white-light emission combining blue conventional fluorescence and yellow TADF from a single compound in various states due to controllable conformational distribution. In addition, dual fluorescence emissions can also be suppressed by improving molecular rigidity to give TADF-dominated emission with efficient reversed intersystem crossing from triplet state to singlet state. Corresponding organic light-emitting diodes (OLEDs) also achieved high efficiencies and reduced efficiency roll-off.

EP06.03.08 Charge Transport and Self-Assembly Tuning by Rational Molecular Design David Wisman1, 2, Tobias Morris1, Christopher Tempas1, Seyong Kim1, Dongwhan Lee1 and Steven Tait1; 1Chemistry, Indiana University, Bloomington, Indiana, United States; 2Materials Analysis, NAVSEA Crane, Crane, Indiana, United States; 3Chemistry, Seoul National University, Seoul, Korea (the Democratic People's Republic of).

Recent trends in the electronics industry have shown that organic semiconductors have the potential to replace silicon in some electronic devices due to their less stringent production environments and ability to offer new functionalities, such as large area flexible and self-healing architectures. Organic semiconductor films have traditionally lagged behind silicon devices due to the difficulty in predicting and controlling the molecular structure, which leads to unpredictable charge transport properties. In traditional organic film materials, the molecules lay flat in the first few molecular layers before transitioning to less favorable geometries for charge transport. Our collaboration has studied a molecular platform, tris(N-phenyltriazole)(TPT), that exhibits planar stacking through >20 molecular layers due to the π-π donor-acceptor intermolecular contacts between the electron-deficient tris(triazole) core and electron-rich molecular peripheral units. Here, we present recent investigations of derivative molecules of TPT, which have different electron distributions and structures, to examine connections between packing structure and charge transport functionality. Molecular-resolution scanning tunneling microscopy is used to compare the molecular packing of these derivative molecules in the monolayer and to investigate the effects the structural and electronic modifications have on the stacking in the multilayer. Conductivity measurements are also made using a 4-point van der Pauw technique to evaluate the charge transport properties of these different molecules compared to an industry standard, pentacene. These results suggest that the TPT molecule and its derivatives are more conductive than that of pentacene. These studies may lead to new organic semiconductor material designs that have well-controlled structure and more predictable charge transport properties, making them more competitive with traditional silicon devices.
Ultra-flat patterning on polymer surfaces on the order of nanometers is extremely important for advances in organic electronics and energy technologies due to improvement of light transmittance at the interface, fine circuit patterning. Nanoimprinting is an effective patterning technique for polymer surface, which has productivity advantages such as simple, low cost, large area. We have previously demonstrated atomic step-and-terrace pattern formed both on soda-lime-silicate glass and polymer sheets such as poly(methyl methacrylate) (PMMA) and polyimide (PI) by the thermal nanoimprint method. In addition this atomic scale morphology contributed to transparent conductive oxide films deposited on nanopatterned PI showed good surface flatness and films deposited on glass resulted in improved crystallinity and crystal orientation [1,2,3]. Meanwhile, we have also reported fabrication of highly oriented and crystallized UV-sensitive oxide semiconductor thin films by an excimer laser annealing at room temperature [4,5], that the technique could improve the crystallinity and orientation of the UV-sensitive semiconductor films on polymer sheets at a temperature lower than the glass transition point of the polymer. In this work we report room-temperature fabrication of UV-sensitive semiconductor thin films such as ZnO or Ga2O3 on the originally developed ultra-flat polymer sheets with 0.3 nm-high atomic step-and-terrace surfaces. Atomic scale surface patterning with a vertical resolution of 0.3 nm was performed on PMMA sheets by thermal nanoimprinting utilizing a mold sapphire (α-Al2O3 single crystal) with atomic step-and-terrace structure on its surface. Thin films of UV-sensitive semiconductors such as ZnO or Ga2O3 were then formed on the patterned PMMA substrates by pulsed laser deposition (PLD) at room temperature. The oriented film revealed flat surfaces reflecting the step-and-terrace morphology on PMMA, having smaller RMS roughness in comparison with the bare substrate.

In addition, XRD results indicated improvement of crystallinity and orientation. The influence of the film structure on the electrical and optical characteristics would also be reported.

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1. G. Tan et al., Nanotechnology 27 (2016) 295603

EP06.03.10 
Roll-to-Roll Deposition Process for Preparing Conjugated Polymer Thin Films 
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Conjugated polymers have a large range of applications, due to their characteristic electronic properties, and the variety of ways they can be processed. However, conjugated polymers with high mobility quickly degrade when processed in air. Therefore, a new roll-to-roll (R2R) processing technique is necessary in order to limit oxidation during polymer processing, while preserving the mechanical and electrical properties of the conjugated polymers.

In our proposed R2R design, polymer solution is slowly pumped onto the surface of a water-filled trough. When the polymer solution contacts the tub, the differing surface tension of the solvent and water causes the polymer solution to quickly spread and dry. The edge of the dry solution is pulled onto a substrate roller, freeing space on the water surface for more solution to spread and dry. This R2R method provides an efficient method for applying small amounts of polymer to large area substrates with minimal waste. Furthermore, the fact that the polymer film is dry when depositing means that it is possible to layer different polymer films onto the same substrate, including materials with non-orthogonal solvents. This is an advantage over other deposition methods, which cannot deposit “wet” solutions onto a dry film because the dry film will re-dissolve with the newly deposited polymer solution.

EP06.03.11 
Crystal Growth Mechanism in Meniscus-Line-Guided Coating Method 
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The meniscus-line-guided coating technique has attracted a lot of attentions in field of organic electronics due to the low fabrication cost and the compatibility with large area processing. Different solution processing approaches such as blade coating, bar coating, zone casting and etc. have been proposed and anealorated to improve the molecular packing in the crystal. To control the crystallinity of the deposited organic semiconductors, the mechanisms behind crystal growth are actually very important. Here, we use blade coating method as a tool to systematically investigate effects of elementary factors on crystal growth rate or mass transfer rate with the semiconductor of 2,7-Dioctyl[1]benzothieno[2,7-b]fluorene BTBT. In the current study, we correlated four elementary parameters including shearing speed, concentration, solvent selection and deposition temperature. We have identified their roles in the meniscus-line-guiding coating process. Shearing speed showed an inverse proportion relationship with resulting thin film thickness, which could be used as thickness modulation parameter while the remained three factors are directly connected to growth rate. The experimental temperature range were set from 30°C to 100°C. By different combination of growth parameters, we achieve a crystal growth rate from 1x10⁻¹¹ to 5x10⁻⁸ cm/s. The equivalent thicknesses are well controlled below 40 nm by adjusting the shearing speed. These results could provide not only deep insight and guidance into crystal growth under meniscus-line-guided coating, but also reference for crystal growth analysis in other research fields.

EP06.03.12 
Comparing Chemical Doping Methods for Preparing Micron-Thick Films of Semiconducting Polymers for Thermoelectric Applications 
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Solution processable semiconducting polymers are of great interest because of their potential for use in a myriad of different device applications. Most recently, their promise for use as thermoelectric materials has come into focus as an area where they might hold significant advantages over their inorganic counterparts. The thermoelectric performance in these materials can be tuned by adjusting the doping level and as such, the molecular doping of conjugated polymer films has become an area of particular importance for these materials. To carry out the doping process, our group employs two different two-step sequential processing techniques, one based on solution processing and the other based on thermal evaporation. The purpose of this talk is to provide a detailed comparison between these two doping methods.

In the first step of the solution sequential processing method, a pristine polymer layer is formed via spin-coating a polymer solution. In the subsequent doping step, a semi-orthogonal solvent is chosen for the dopant that swells but does not dissolve the underlying polymer layer. The dopant is then driven homogeneously inside the swollen polymer film by spin-coating the dopant solution on top of the pre-formed polymer underlayer. Because this solution-based method relies on the polymer layer swelling in the presence of a semi-orthogonal solvent, dopant intercalation is largely independent of the polymer layer thickness, provided the solvent fully penetrates throughout the extent of the polymer layer. For the evaporation sequential doping method, thermal evaporation is used to place the dopant on top of the pre-existing polymer layer, where heating of the underlying polymer film is often used to help intercalate the dopant inside the polymer film from the gas phase. To date, most studies investigating doping by this process have been carried out on ultra-thin polymer films on the order of ~20 nm in thickness. For practical use, much thicker device architectures must be implemented and it has until now remained a mystery how this evaporative doping process would scale to multi-micron thick films for thermoelectric applications.

Here, we perform a systematic comparison between these two techniques by examining infiltration of the dopant 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) inside increasingly thick polymer films of poly(3-hexylthiophene-2,5-diyl) (P3HT). Structural changes induced by the incorporation of the dopant species are evaluated using grazing-incidence wide-angle x-ray scattering (GIWAXS). In addition, changes in inter and intralayer ordering of the low-energy polaron absorption band are measured as a way of characterizing the degree of free charge carrier delocalization. Finally, conductivity measurements, coupled with measurements of the Seebeck coefficient, illuminate how the thermoelectric power factor changes as increasingly thick polymer films are used. We find, quite surprisingly, that the power factor obtained for these materials with the two different doping methods are largely indistinguishable, and even approach the same level within the error of the measurement at increasing film thicknesses. Thus, when thermal evaporation is undesirable due to constraints in cost or time, solution processing provides a suitable method of dopant intercalation for fabricating polymer-based thermoelectric devices.
Electrode ignorant substrates (EGTs) or electric double layer transistors (EDLTs) have attracted significant research attention as potential switching devices for wide variety of thin-film devices because of their solution processability, low-voltage operations, and excellent device performance. Many different types of organic and inorganic semiconductors have been applied for these high performance EGTs. In this work, organic/inorganic hybrid complimentary inverters operating at low voltages were successfully fabricated by transfer-stamping all the active components including organic p-type poly(3-hexylthiophene) (P3HT), inorganic n-type zinc oxide (ZnO), high capacitance solid electrolyte ion gel dielectric and conducting polymer. A semicrystalline homopolymer-based gel electrolyte was transfer-stamped on the semiconductors for low voltage EGT operation. For the ionogel stamping, the thermoreversible crystallization of network cross-links was utilized to control the physical contact between the gel and the semiconductors. The p-type P3HT EGTs showed high hole mobility of 2.14 cm²/Vs, whereas the n-type ZnO EGTs exhibited high electron mobility of 1.82 cm²/Vs. By combining these p- and n-type EGTs in series, organic/inorganic hybrid complimentary inverters were fabricated. The complementary inverter operated at low-voltages below 2 V with appropriate inversion characteristics including a high voltage gain of ~18.

EP06.03.14
Two-Dimensional Organic Single Crystals as Deposition Templates for High-Performance Field-Effect Transistors Zhiwen Zhou, Shien-Ping Feng and Paddy K. L. Chan; The University of Hong Kong, Hong Kong, Hong Kong.

In a bottom gate top contact organic field effect transistors (OFETs), the carrier transportation is happening in the first few monolayers of organic semiconductors closed to the dielectric/semiconductor interface. Great efforts have been devoted to modifying the physical properties of the dielectric-organic interface, including improvement of conductivity by doping and enhancement of crystallinity by optimizing the molecule packing and reducing grain-boundary defects. Here, we firstly fabricated a two-dimensional (2D) highly crystalline C_60-DNTT film with large-area uniformity by a quasi-steady ultra-slow shearing (USS) method where the heterogeneous nucleation is intentionally chosen with a significant reduction of the number of nuclei. The preferential molecular orientation during the process was observed and the behind formation mechanism was analyzed in the form of surface energy calculated by density functional theory (DFT). After having the 2D crystal being deposited, we further demonstrated the following thermally deposited C_60-DNTT ultra-thin film can pack in a particular form by using the 2D crystalline monolayer as a template. The sequentially deposited films showed an excellent crystallinity with a followed crystal orientation of templating crystals through a vertical quasi-epitaxial growth mode. Being benefited from the solution shearing layer, the OFETs with hybrid-deposited organic semiconducting films exhibited an improved carrier mobility of 19.7 cm²/Vs compared with 2.5 cm²/Vs achieved by solely thermal-evaporated thin-film devices. In turn, the overlying films act as a passivation layer and help to gain a better long-term stability over one year with only 5-10% drop of carrier mobility. This work provides a simple and easy approach for fabricating high-performance and low-cost electronics on a large scale by seeded growth templates.

EP06.03.15
Liquid Crystal- Organic Field Effect Transistor with Elastomeric Gate Dielectric Reshma Ravendran,1,2, Mamatha Nagaraj1 and Manoj A. Namboothiry1; 1School of Physics, Indian Institute of Science Education and Research-Thiruvananthapuram, Thiruvananthapuram, India; 2School of Physics and Astronomy, University of Leeds, Leeds, United Kingdom.

The basic attraction of organic electronic devices is their flexibility. Among the widely used flexible materials, the polymer elastomer, poly(dimethylsiloxane) PDMS has an important position due to its additional features like optical transparency and insulating properties. In our recent work, the effective application of PDMS as a gate dielectric in solution-processed organic field effect transistors (OFETs) was investigated.1 In the present work, we discuss the fabrication of OFETs using a solution-processed liquid crystal (LC) semiconductor, 2-decyldodecyl-4,7-(phenyl-1-[benzozeno[3,2-b][1]benzothiophene (Ph- BTBT-10) with PDMS as the gate dielectric. The organic semiconductors exhibiting liquid crystalline phase have attracted high attention due to their capability to self-organize into large area thin films by solution processing methods and their high charge transport properties.2–3 Ph- BTBT-10 exhibiting smectic phases is attractive due to its solution processability and its good thermal stability up to 250°C and high mobility of 13.9 cm²/Vs.2 Here, the high potential of Ph- BTBT-10 as an active organic material is utilized to fabricate LC-OFETs with PDMS as gate dielectric material. The devices showed high performance with an average field effect mobility > 5 cm²/Vs and current on/off ratio as high as 10⁶. These devices worked under very low threshold voltage (<5 V) which indicates the capability of elastomers for flexible OFET applications. The high device performance is attributed to the good crystallinity of the LC thin-film solution-casted on PDMS surface. Also, the LC material maintained its bilayer structure throughout the OFET operation.

References:

EP06.03.16
Fabrication and Characterization of Nano Particle Colors for Electrophotoreic Display Sung Yong Nam; Gyeongsang National University, Jinju, Korea (the Republic of).

Electrophoretic display (EPD) technology is a technology which has lots of advantages such as easy manufacturing process, being made of flexible material, requiring ultra-low power consumption, low-cost manufacture and, most of all, easy and convenient to read. In this study nano-size color particles were studied for application to electrophoretic display. Color particles were prepared by Emulsion polymerization and Seed polymerization. Polymerization method were proposed for the synthesis of monodispersed poly(vinyl acetate-co-divinylbenzene) [poly(VA-co-DVB)] particles with different VAc/DVB feed ratios. Poly(Vinyl alcohol-co-divinylbenzene) [poly(VAc-co-DVB)] particles were obtained by the basic hydrolysis of poly(VAc-co-DVB) particles. The hydroxyl groups on poly(VA-co-DVB) particles have a suitable reactive functionality for surface covalent bond with reactive dye. So, Poly(VA-co-DVB) particles were reacted with reactive dye. Poly(VA-co-DVB) color nano particles were characterized by using SEM, IR, DSC, UV-vis.

EP06.03.17
Improved Hydrophobic Interface of Polyurethane Acrylate via Perfluoropolyether for Efficient Transfer Printing and Stable Operation of Conductive Polymer in Perovskite Photovoltaic Cells Min Ji Yi, Ji Hyun Lim, Min Seong Kim and Dongs Hwan Wang; Chung-Ang Univ, Seoul, Korea (the Republic of).

Recently, development trends of electronic devices and optoelectronic devices are related to simple and economic next generation printing processes based on organic and organic/inorganic hybrid nano materials. The transfer printing process, which is one of the next generation printing processes, is attracting attention because it is relatively dry, economical, and more stable by forming a reverse structure compared to the wet process. In this research, we investigated transfer printing process from enhanced hydrophobic interface of polyurethane acrylate (PUA) mold film via perfluoropolyether (PFPE)3. The energy release rate (G) of mold film has been successfully controlled for efficient transfer process, which was confirmed by contact angle measurement compared to the normal PUA. The transfer printed PEDOT:PSS layer exhibits comparable surface properties, and also induce favorable crystallinity of perovskite related to the spin-coated layer, which shows similar JSC and PCE (spin-coated vs. transfer printing: 12.85 VS. 12.33 %), and improved VOC. Furthermore, the stability of the device with transfer printed PEDOT:PSS layer was confirmed by the preserved crystallinity of perovskite, and the inhibition of the degradation of ITO from XRD and XPS analysis, respectively. As a result, the transfer-printed hole extraction layer through interface control between mold film and PEDOT:PSS using the improved hydrophobicity contributes to maintaining the surface morphologies and device electrical properties, which correlates with the stable operation of perovskite photovoltaics. This work suggests a encouraging process of organic inter-layer fabricated by the controllable material-customized transfer films.

Solution-processed active semiconductor doping would be a powerful strategy in order to improve CNTFETs performance in balanced charge transport. CNTs are promising material for high performance, large area printable and flexible thin film transistor. However, as synthesized single-walled carbon nanotubes (SWNTs) show non-uniform electrical properties due to the mixture of metallic and semiconducting SWNTs. Selective separation of semiconducting SWNTs (s-SWNTs) using conjugated polymers has been developed with the aim of utilizing their superior properties. We separated s-SWNTs with the high purity from as-grown mixed-type SWNTs using conjugated polymer with long alkyl side-chain length. Separated s-SWNTs were adapted for active layer of CNTFETs with or without dopant. Properties and doping effects of the CNTFETs active layer were revealed by UV-VIS spectroscopy, Raman Spectroscopy, low-temperature measurements and other experiments. We demonstrate that hole and electron charge carrier tuning can be easily achieved by simple spin coating in CNTFETs with s-SWNT/dopant bilayer structure. Furthermore, through this study, we implemented logic gates such as inverter and pass gate with simple solution processing.

**EP06.03.19**
Efficient Deep-Blue Organic Light-Emitting Diodes with Asymmetric Diphenylsulfone-Type Materials Used as TADF Emitter and Sensitizer

Hui Jae Choi, Ohyoung Kim, Seok-Ho Hwang, Chul Won Lee and Byung Doo Chin; Dankook Univ, Yongin, Korea (the Republic of).

The state-of-the-art commercial materials of organic light emitting diode (OLED), especially for a blue fluorescence, still need further improvement in terms of their efficiency. We have synthesized several diphenylsulfone-type thermally delayed activated fluorescence (TADF) host materials with diphenylsulfone (DPS) as acceptor unit, while carbazole (Cz), 3,6-di-tert-butyl-carbazole (tBCz), or 7,7-dimethyl-5,7-dihydroindeno[2,1-b]carbazole (DMICz) were utilized as donor units. The calculated S1/T1 energies of synthesized host materials, CzBrCz-DPS and CzDMICz-DPS (with the standard B3LYP/6-31G*) are 3.35/3.00 eV and 3.13/2.86 eV, respectively. Deep blue emitting TADF devices with a color coordinate of (0.16,0.09) and (0.15,0.09) were obtained for devices having CzBrCz-DPS and CzDMICz-DPS emitter with bis(2-(diphenylphosphino)phenyl) ether oxide (DEPEO) host. A molecular design of interlocking two phenyl units of DPS could help to reduce molecular motion, resulting in a shift of emission color to deep blue. Experimental values of electro-optical properties and time-resolved studies were investigated by the spectrometry on photoluminescence, UV-vis, and transient experiment to analyze a good overlap of the host emission to dopant absorption and delayed fluorescence. Therefore, those TADF devices demonstrated still limited efficiency, about 3.7% (DPEPO): CzBrCz-DPS (10%) and 5.7% (DPEPO): CzDMICz-DPS (10%). For a further improvement of TADF device efficiency, severe roll-off characteristics, and poor device stability, asymmetric DPS series compounds were applied for sensitizing host at TADF device architecture. The hyperfluorescence devices, with blue emitting layer composed of DPEPO: DPS-series-sensitizers (30%):fluorescent dopant (5,9-Diphenyl-5H,9H-[1,4]benzazaborinio [2,3,4-k]phenazaborine; DABNA-1; 1%), showed 12 to 14% external quantum efficiencies at a color coordinate about (0.14, 0.07) depending on the type of asymmetric DPS-series-sensitizers. Although more detailed investigation is required, it is expected that sensitizers with tBCz-donor group were found to be more efficient compared with DMICz-donor materials.

**EP06.03.20**
The Effects of Annealing on Doped P3HT Thin Films for Potential Electronic Applications

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Polymer conjugated materials are convenient for developing future soft-material-based semiconductors, conductors, electronic and optoelectronic devices due to their inherent features. These features include being lightweight, flexible, cost efficient, malleable, and easily scaled. Similar to their inorganic counterparts, the addition of certain minority molecules, or dopants, to polymer conjugated materials can significantly alter the electronic and optoelectronic properties of the host conjugated polymers or composites. This allows for tunability of a variety of electronic and optoelectronic applications. One way to improve device performance is through the process of thermal annealing. Annealing allows for a polymer matrix to self-assemble into a lower energy state, which leads to an increase in crystallinity and higher charge mobility. Previous research does not explicitly define how dopants can affect this process. This study involves an evaluation of the affects of annealing with doped P3HT films to demonstrate changes in optoelectronic and electronic properties.

**EP06.04.01**
Device Physics of Non-Ideal Organic Thin-Film Transistors and Analysis of Current-Voltage Relations

Chuan Liu; School of Electronics and Information Technology, Sun Yat-sen University, Guangzhou, China.

Very high values of carrier mobility have been recently reported in newly developed materials for field-effect transistors (FETs) or thin-film transistors (TFTs). Concerning the precise characterizations of OTFTs or OFETs, we investigate the device physics of devices with non-ideal current-voltage relations:

(a) How to choose the analysis tool for contact resistance in OTFTs? Given the limitation of the transfer-line method in the difficulty in experiments and theoretical assumptions, we could perform analysis on a single device with transfer or output characteristics. These methods provide facile tools and whether their assumptions are valid are discussed.

(b) How much contact resistance a FET or TFT can tolerate allowing the conventional current-voltage equations? Mobility in transistors with resistive contact can be underestimated with the presence of the injection barrier, whereas mobility in transistors with gated Schottky contact can be overestimated by more than ten times. This is because the band bending and injection barrier experience a complicated evolution on account of electrostatic doping in the semiconducting layer.

(c) How to assess the capacitance in OTFTs or OFETs, we investigate the device physics of devices with non-ideal current-voltage relations: we could perform analysis on a single device with transfer or output characteristics. These methods provide facile tools and whether their assumptions are valid are discussed. Underestimated with the presence of the injection barrier, whereas mobility in transistors with gated Schottky contact can be overestimated by more than ten times. This is because the band bending and injection barrier experience a complicated evolution on account of electrostatic doping in the semiconducting layer.

(d) How to compare disorders of charge transport in various OSCs can be directly compared in the same map? The generalized Einstein relation can unify various theoretical models and predict charge transport in OSCs with various crystallinity, by altering the variance of the density of states and delocalization degree in a Gaussian-distributed density of states.

Very high values of carrier mobility have been recently reported in newly developed materials for field-effect transistors (FETs) or thin-film transistors (TFTs). Concerning the precise characterizations of OTFTs or OFETs, we investigate the device physics of devices with non-ideal current-voltage relations:

(a) How to choose the analysis tool for contact resistance in OTFTs? Given the limitation of the transfer-line method in the difficulty in experiments and theoretical assumptions, we could perform analysis on a single device with transfer or output characteristics. These methods provide facile tools and whether their assumptions are valid are discussed. Underestimated with the presence of the injection barrier, whereas mobility in transistors with gated Schottky contact can be overestimated by more than ten times. This is because the band bending and injection barrier experience a complicated evolution on account of electrostatic doping in the semiconducting layer.

(b) How much contact resistance a FET or TFT can tolerate allowing the conventional current-voltage equations? Mobility in transistors with resistive contact can be underestimated with the presence of the injection barrier, whereas mobility in transistors with gated Schottky contact can be overestimated by more than ten times. This is because the band bending and injection barrier experience a complicated evolution on account of electrostatic doping in the semiconducting layer.

(c) How to assess the capacitance in OTFTs or OFETs, we investigate the device physics of devices with non-ideal current-voltage relations: we could perform analysis on a single device with transfer or output characteristics. These methods provide facile tools and whether their assumptions are valid are discussed. Underestimated with the presence of the injection barrier, whereas mobility in transistors with gated Schottky contact can be overestimated by more than ten times. This is because the band bending and injection barrier experience a complicated evolution on account of electrostatic doping in the semiconducting layer.

(d) How to compare disorders of charge transport in various OSCs can be directly compared in the same map? The generalized Einstein relation can unify various theoretical models and predict charge transport in OSCs with various crystallinity, by altering the variance of the density of states and delocalization degree in a Gaussian-distributed density of states.

References:

[4] Submitted
is typically employed in OPVs that is processed almost exclusively from toxic organic solvents, such as chloroform, chlorobenzene, and 1,2-dichlorobenzene. There is the need to move away from processing with chlorinated solvents and hence the development of eco-friendly processing technologies for solar cells is a recent target of the polymer solar cell community. Unfortunately, a reduction in solar cell performance often results when chlorinated solvents are eliminated, which is attributed to the non-optimal microstructure of the light absorbing layer. This seminar presents recent work on unravelling the material-morphology-performance relationships in eco-friendly processed polymer solar cell photoactive layers with the use of advanced synchrotron X-ray characterization techniques, STXM and NEXAFS. Here we explore the microstructure of green solvent cast BHI films and aqueous colloidal nanoparticle films for the poly[2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diy-alt-thiophene-2,5-diyl] (TQ1) : phenyl-C61-butyric acid methyl ester (PC61BM) and poly(3-hexylthiophene) (P3HT) : PC61BM donor-acceptor material systems. With additive engineering and customizing nanoparticulate colloidal inks we are able to reduce the material domain size to approach the typical exciton diffusion length in these organic semiconductor systems, demonstrating that eco-friendly processing of large area OPV is a realistic goal for the near future.


8:45 AM EP06.04.03
Developing Atomic-Scale Models to Improve the Processing of Organic Semiconductors
Shi Li; Sean Ryno and Chad Risko; Chemistry, University of Kentucky, Lexington, Kentucky, United States.

To ensure optimal performance, the development of organic semiconducting materials from their molecular and/or polymer constituents requires precise processing controls to optimize the solid-state molecular packing arrangements. Temperature, solution deposition rates, and secondary solvents are among the tools that can be used to fine tune solid-state packings. However, many of these tools are used in an ad hoc fashion, and process discovery remains largely in the realm of trial-and-error approaches. We are developing all-atom molecular dynamics (MD) approaches to explore the solution processing of organic semiconductors. Here we will discuss recent advances in simulations that examine the free energies of mixing of solutions, and the influence of solution composition on molecular conformations and aggregation. For solvent and additive systems, diffusion parameters, solvation energies, and free energies of mixing are determined to provide insight into the solution environment. We then use these solvent systems to explore the solution behavior of complex donor-acceptor oligomers. The simulations reveal critical insight into the role of the secondary solvent additive during aggregation. These simulations are providing key atomic-scale insights as to how variations in processing solutions impact morphology development in organic semiconductors.

9:00 AM *EP06.04.04
Formation and Device Implications of Microcrystalline Organic Semiconductor Films and Heterojunctions
Barry P. Rand; Princeton University, Princeton, New Jersey, United States.

We have recently been exploring organic semiconductor-based thin films that feature crystalline grains of up to 1 mm in extent, termed microcrystalline films. We will show our efforts to understand their formation, epitaxy, and transistors. Homoeptaxial studies uncover evidence of point and line defect formation in rubrene films, indicating that homoepitaxy is not at equilibrium or strain-free. Point defects that are resolved as screw dislocations can be eliminated under closer-to-equilibrium conditions, whereas we are not able to eliminate the formation of line defects. We are, however, able to eliminate these line defects by growing on a bulk single crystal of rubrene, indicating that the line defects are a result of strain built into the thin film template, indicating that, perhaps in general, organic crystalline thin films may not adopt the exact lattice of a bulk crystal.

In terms of optoelectronic behavior, we have found that charge transfer (CT) states incorporating these long-range-ordered films can be highly delocalized, contributing to noticeably lower energy losses. Also, we have discovered that relative energies of CT states with respect to singlet and triplet energy levels are critical when considering devices that exploit multiple exciton processes such as singlet fission and its complement, triplet-triplet annihilation (or triplet fusion). We will discuss these aspects and their implications for more efficient organic solar cell function.

9:30 AM BREAK

9:45 AM *EP06.04.05
Ionic Conduction as a Function of Side-Chain Chemistry of Polythiophene Derivatives
Christine Luscombe; University of Washington, Seattle, Washington, United States.

A new class of materials called mixed ionic/electronic conductors (MIECs) has the potential to be highly useful for many applications, ranging from biological sensors to battery electrode materials. The majority of current organic MIECs are created through the blending of two materials, where one component provides ionic conductivity, and the other electronic. This leads to a complex phase behavior that is still not fully understood. For rational design of MIECs, the connection between morphology and conduction must be better understood. To begin to answer these questions, guided by molecular dynamics simulations we synthesized two polythiophene derivatives bearing oligoethylene glycol side chains; one with an oxygen atom directly conjugated to the thiophene backbone, and one with a methylene spacer. Both polymers showed lithium uptake into crystalline domains, though lithium preferentially resided in the amorphous regions. By using a combination of electrochemical impedance spectroscopy and molecular dynamics simulations, we confirmed that ionic conduction occurs predominately in the amorphous regions. These polymers provide a valuable scaffold into investigating the interplay of morphology and ionic conduction.

10:15 AM EP06.04.06
Disregarded Channel Fringe Effect on Mobility Overestimation in Organic Thin-Film Transistors
Ke Pei and Paddy K. L. Chan; The University of Hong Kong, Hong Kong, Hong Kong.

Field-effect carrier mobility (m) is an important parameter to evaluate the performance of the organic field effect transistors (OFET). However, accurate measurement of this value is nontrivial. Apart from the recently discussed Schottky contacts induced mobility overestimation, the fringe effect resulting from the improper electrodes design is another disregarded source which would lead to mobility overestimation even the devices show good linearity in the transfer curves. We found that the OFET with unpatterned active layers or gate dielectric can have a mobility overestimation up to 210%. We systematically examine the fringe effect on mobility overestimation in the organic transistors with both vacuum-deposited and solution-processed semiconductor active layers. We introduce a correction-factor (C-factor) of the W/L defined by the source-drain electrodes to indicate the severity of the mobility overestimation caused by the fringe channel. By using electrodes with W/L ratio equals to one, the C-factor can reach 1.16 and 0.74 for vacuum-deposited and solution-processed OFETs, respectively. On the other hand, we also demonstrated the C-factor can be minimized to 0.1 when using properly designed electrodes (W/L ≥ 40 for vacuum-deposited and W/L ≥ 20 for solution-processed transistors). In the talk, we will also provide recommendations on the design of device geometry and channel dimension so that common pitfalls of fringe effect in the device fabrication can be avoided. With a detailed comparison table of the reported mobilities, the current work will help to provide a blueprint to the researchers about how the fringe effect would affect the reliability of reported mobility values. We believe the improvement on accurate evaluation of carrier mobility in relation to the fringe effect will ensure the development of novel OFET materials towards a correct direction, rather than keep on reporting inflated mobility values which are actually wrong.

10:30 AM EP06.04.07
In Situ Measurement of Evolving Exciton Dynamics During Organic Film Formation
Cathy Y. Wong; University of Oregon, Eugene, Oregon, United States.

The electronic structure and exciton dynamics of the molecules and polymers that form the active layer in organic electronic devices can change dramatically during solution deposition. As solvent vaporizes, molecules become electronically coupled as they aggregate to form a film, sometimes dramatically changing the exciton dynamics and thus the suitability for electronic devices. The dynamics of molecules in solution and in thin films of aggregates can be measured using transient absorption spectroscopy, but the exciton dynamics of intermediate aggregation states during thin film formation are typically unknown since measurements cannot be performed quickly enough to collect accurate
transient absorption spectra of these species. The exciton dynamics of evolving material systems can be measured by increasing the speed of data collection. A novel implementation of transient absorption spectroscopy is introduced that can measure transients with up to a 60 ps pump-probe time delay in one shot. The exciton dynamics measured during the solution deposition of a film is validated by comparing the initial exciton dynamics of the solution and the final exciton dynamics of the dry film to traditional transient absorption measurements. The exciton dynamics of intermediate aggregation states will be presented for the first time. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for particular types of electronic devices.

10:45 AM EP06.04.08
The Impact of Energy Barriers at Grain Boundaries and Interfacial Traps on Charge Carrier Motion in a High-Mobility, sub 10 nm Thin, Organic Semiconductor
Thomas Weitz, LMU Munich, Munich, Germany.

Using high-surface tension solvents allowed us to grow 3–10 nm thick, highly-crystalline films of a N,N-di(5-tert-butylphenyl)-1,7(6)-dicyano-perylen-3,4,9,10-bis(carboximide) (PDI1MPCN2) at the liquid/air interface of a drying droplet [1]. We find, that charge carrier mobilities in these electron conductive films is as high as 4 cm^2/Vs even for an only 3 nm thin PDI1MPCN2 film. Changing the solvation composition used for crystallization of our organic semiconductor also has allowed us to systematically tune the crystallinity and consequently the grain boundary density in thin films. From the temperature-dependent charge carrier mobility, we have extracted the density of states and compared to it to kinetic Monte Carlo simulations [2]. This combined theoretical and experimental approach has allowed us to identify, that it is rather the energetic barriers at grain boundaries than the usually identified energetic traps that limit charge carrier motion below room temperature. We also have revealed that the dipole moment of the PDI1MPCN2 is the cause for the energetic disorder at grain boundaries serving as clear guideline for future design of organic semiconductors with potentially no energetic barriers present at the grain boundaries. We furthermore have investigated in detail the dependence between charge carrier mobility and density at various temperatures and find surprisingly that above room temperature the charge carrier mobility decreases upon increasing the charge carrier density [3]. While the true cause for this suppression is currently unclear, we present evidence that the squeezing of charges closer to the semiconductor/dielectric by the gate dielectric field a subsequent scattering at this interface might cause the drop in mobility. We anticipate that our combined observations will help to understand the still debated nature of charge transport in high-quality organic semiconductors.


11:00 AM EP06.04.09
Selective Poling the Ferroelectric Dielectric Layer in Organic Field-Effect Transistors for Improved Performance
Amrit Laudari, Alec M. Pickett and Suchismita Guha; Physics, University of Missouri, Columbia, Missouri, United States.

Polymer ferroelectrics are playing an increasingly active role in flexible memory application and wearable electronics. The relaxor ferroelectric dielectric, poly(vinylidene fluoride trifluoroethylene) (PVDF-TrFE), although vastly used in organic field-effect transistors (FETs), has issues with the gate leakage current especially when the film thickness is below 500 nm, and low carrier mobilities that arise due to its inherent polarization fluctuation. The poling condition of PVDF-TrFE in organic FETs plays a large role in dictating the transport properties. The subthreshold swing and other transistor parameters in organic FETs can be controlled in a reversible fashion by switching the polarization direction in the PVDF-TrFE layer [1]. By using solution processed small molecule semiconductors such as bis(dicarboximide) (PDI1MPCN2) at the liquid/air interface of a drying droplet [1]. We find, that charge carrier mobilities in these electron conductive films is as high as 4 cm^2/Vs even for an only 3 nm thin PDI1MPCN2 film. Changing the solvation composition used for crystallization of our organic semiconductor also has allowed us to systematically tune the crystallinity and consequently the grain boundary density in thin films. From the temperature-dependent charge carrier mobility, we have extracted the density of states and compared to it to kinetic Monte Carlo simulations [2]. This combined theoretical and experimental approach has allowed us to identify, that it is rather the energetic barriers at grain boundaries than the usually identified energetic traps that limit charge carrier motion below room temperature. We also have revealed that the dipole moment of the PDI1MPCN2 is the cause for the energetic disorder at grain boundaries serving as clear guideline for future design of organic semiconductors with potentially no energetic barriers present at the grain boundaries. We furthermore have investigated in detail the dependence between charge carrier mobility and density at various temperatures and find surprisingly that above room temperature the charge carrier mobility decreases upon increasing the charge carrier density [3]. While the true cause for this suppression is currently unclear, we present evidence that the squeezing of charges closer to the semiconductor/dielectric by the gate dielectric field a subsequent scattering at this interface might cause the drop in mobility. We anticipate that our combined observations will help to understand the still debated nature of charge transport in high-quality organic semiconductors.

We acknowledge the support of this work through the National Science Foundation under Grant No. ECCS-1707588


11:15 AM EP06.04.10
Dynamic Mechanical Analysis of Polymer Semiconductors for Insights into Mechanical Stability
Nuppal Balar1, Masoud Ghasemi2, Harold Ade3 and Brendan T. O'Connor; 1Physics, North Carolina State University, Raleigh, North Carolina, United States; 2Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, United States; 3North Carolina State University, Raleigh, North Carolina, United States.

One of the key advantages of polymer semiconductors over traditional inorganic semiconductors is their mechanical behavior. The polymers typically have lower stiffness, greater ductility and toughness than their inorganic counterpart enabling effective integration in ultraflexible and stretchable devices. To exploit the full potential of these materials for mechanically demanding applications, the fundamental thermomechanical behavior of these materials must be accurately determined, including how their viscoelastic properties translate to device stability. However, capturing the thermomechanical properties of these materials can be challenging. A common approach is to use differential scanning calorimetry (DSC). But, DSC often doesn’t have the sensitivity to capture the thermal transitions of polymer semiconductors. Dynamic mechanical analysis (DMA) on the other hand offers a very sensitive and versatile tool to probe the thermomechanical behavior of these materials. In this talk, we describe specimen preparation on probing both bulk and thin film thermomechanical properties of the polymers. We demonstrate DMA measurements that reveal thermal transitions including sub-glass transitions in a number of high performance polymer semiconductors, and how these transitions relate to the film mechanical behavior such as ductility, toughness, and creep. The implications of these properties on mechanical stability of devices will then be discussed. Furthermore, we demonstrate that the thermomechanical behavior of polymer-smaller molecule blends used in high performance solar cells is directly related to the long term device stability. We show that the small molecule diffusion measured by secondary ion mass spectroscopy can be directly related to thermal transitions, and how this dictates the blend film properties needed to ensure long-term morphological stability.

11:30 AM EP06.04.11
Polymer Ordering in Monolayers and Thin-Films Allowed to Reach Local Equilibrium
Hansard Ade; Department of Physics and Organic and Carbon Electronics Lab (ORACEL), North Carolina State University, Raleigh, North Carolina, United States.

Although it is well known that intra- and intermolecular ordering greatly impact the electronic and optoelectronic properties of semiconducting polymers, the interrelationship between ordering of alkyl sidechains and conjugated backbones has not yet been fully detailed. A recent discovery clearly demonstrated that the tendency of the side-chains and the backbone to order is not synergistic [1], rather a competition was observed in six representative semiconducting polymers. The ordering of the respective polymer components is monitored by NEXAS, UV-vis spectroscopy, as well as diffraction and exhibits distinct signatures. Overall, a vertically layered multilayer nanostructure with ordered side-chain similar to classic semiconducting heterostructure bulk epitaxy. In other words, we need to design materials as completely ordered crystals and not partially ordered sublattices.

1:30 PM *EP06.05.01
From Molecular Design to Materials Properties—Developing Theoretical Tools to Aid in the Development of Organic Semiconductors
Chad Risko; University of Kentucky, Lexington, Kentucky, United States.

The design of molecules and polymers for solution-deposited organic semiconductor materials generally considers the chemical modulation of (i) the π-conjugated backbone to modify the electronic and optical characteristics and (ii) the alkyl side chains to govern solubility. As the solid-state material forms, physical interactions among these constituents play important, yet not well understood, roles in directing the molecular-scale packing arrangements that in part determine the final material properties. Further, the functions of the processing solutions are not clear, adding yet another layer of complexity in determining how materials self-assemble. In this presentation we will discuss the development of atomic-scale models that invoke thermodynamic, kinetic, and quantum-chemical methods to deliver insights into the processing and solid-state packings of organic semiconductors. The chemical knowledge developed through these investigations is beginning to refine and offer novel understanding essential to the development of next-generation organic semiconductor active layers, and is opening new pathways for in silico materials development.

2:00 PM EP06.05.02
Towards Data-Driven Explorations of Molecular Organic Semiconductors
Qianxiang Ai; Sean Ryno and Chad Risko; University of Kentucky, Lexington, Kentucky, United States.

Though organic semiconductors have illustrated their potential as industry-relevant materials for electronics applications, there are few guidelines that can take one from designing molecules to constructing functional materials. Relatively weak, non-covalent intermolecular interactions determine the thermodynamic preferences for solid-state packing, while interface interactions and kinetic factors during processing also play important roles. For crystalline materials, crystal structure prediction remains a grand challenge, with an even greater challenge stemming from the need to predict and control the formation of the particular crystal polymorph that provides the best materials characteristics for a given application. Such predictive capabilities, which need to span and draw correlations from the atomic to the macro-scale, will require a united effort from researchers across multiple disciplines.

To address some of these challenges, we have initiated the construction of a database as a digital platform aiming to serve the community with a high-throughput computational workflow and a web-based user interface. Featuring combinatorial inputs from synthetic chemists, theoreticians, experimentalists, and device physicists, the database employs a descriptor-based scheme to explore the correlations between molecules, their solid-state packings, and materials properties. Here, we illustrate database utility through the investigation of functionalized acenes as we refine the structure-packing model that has been proposed to offer predictive capabilities for this materials class.

2:15 PM EP06.05.03
Critical Role of Electron-Donating Thiophene Group on the Thermomechanical Property of Donor-Acceptor Semiconducting Polymers
Song Zhang and Xiaodan Gu; Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi, United States.

Organic semiconducting polymers are promising candidates for stretchable electronics for their mechanical compliance. Donor-Acceptor type conjugated polymers have been the key drive for recent boost in device performance. Up to date, the effect of the conjugated backbone building block on the thermomechanical property of conjugated polymers has not been carefully studied, despite much work on their influence on the electronic property. In this talk, I will discuss our work on the structure and thin film thermomechanical property relationship for donor-acceptor polymers with systematically varied donor units on the conjugated polymer. To characterize the thermomechanical performance, the pseudo-free standing tensile test was used to obtain the full stress-strain curve. The glass transition temperature was measured for both thin and bulk films using AC-chip calorimetry and DMA, respectively. Thin film morphology was detected using AFM, UV-vis, and GIWAXS for further understanding. OFET devices were fabricated to test the electronic performance. The backbone structure and thermomechanical property relationship was established and applied to the design of new stretchable conjugated polymers.

2:30 PM BREAK

3:30 PM *EP06.05.04
Non-Conjugated Radical Polymers as Transparent Conductors in Organic Electronic Devices
Bryan W. Boudouris; Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana, United States.

Radical polymers are an emerging class of organic electronic materials that are composed of a non-conjugated macromolecular backbone and with stable open-shell moieties present on their pendant groups. These oxidation-reduction-active (redox-active) macromolecules have been oft-used in the realm of electrolyte-supported energy storage devices due to the rapid reaction kinetics associated with the oxidation and/or reduction of the high densities of radical sites present along the polymer chains. To date, their utilization in solid-state organic electronic devices has been limited due to the lack of conjugation along their macromolecular backbone and the idea that this lack of conjugation necessarily limits their ability to conduct charge effectively in the solid state. Here, we demonstrate that radical polymers, in fact, are able to achieve relatively high electrical conductivity values (i.e., > 20 S m⁻¹) if appropriate molecular design criteria are met.

Specifically, two key design rules exist for radical polymers, and these design rules are distinctly different from what is observed in common conjugated semiconducting and conducting polymers. First, in order to ensure that there is a high density of redox-active sites by which to pass charge in the solid state, radical polymers must be synthesized in such a manner that the fraction of pendant groups that have an open-shell character to them approaches unity. While a fairly stringent requirement, this can be accomplished in a straightforward manner by utilizing polymerization schemes that do not follow a radical-mediated pathway. Second, the glass transition temperature of the radical polymer must be lower than the degradation temperature of the radical polymer. This allows for thermal annealing of the radical polymer after it has been cast into a thin film. Through a combination of experiment and computation, we demonstrate that this annealing process is crucial to the formation of a thermodynamically-stable nanoscale structure that allows for electronic communication between the radical pendant groups. When these two design criteria are met, we have been able to demonstrate electrical conductivity values for tailored radical polymers in excess of 20 S m⁻¹. This places our pristine (i.e., not doped) radical polymer electrical conductivity on par with many common commercial grades of doped conjugated polymers [e.g., poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS)]. In addition to the device stability benefits associated with a lack of acidic dopants, the non-conjugated macromolecular backbones necessarily allow for high optical transparency values to be achieved across the visible spectrum for our radical polymers. For all of these reasons, radical polymers present themselves as useful materials in myriad optoelectronic and sensing device applications, and they offer the promise of replacing the current state-of-the-art of transparent conducting polymers and composite materials.

In particular, we will describe how specific nitroxide-based radical polymers are implemented as next-generation organic electronic materials in organic photovoltaic (OPV) devices and perovskite solar cells; organic field-effect transistors (OFETs); electrochromic devices; and bioelectronic sensors. The inclusion of the radical polymer layer improves uniformity of charge transport and reduces the contact resistance in the device. Finally, the high transparency in the visible spectrum allows for high-performance electrochromic devices that exhibit relatively rapid switching rates and are stable for a large number of cycles. Thus, we aim to show that radical polymers allow one to tie molecular design directly to device performance in a relatively linear manner.
High Sensitivity Ion-Selective Organic Electrochemical Transistor

EP06.05.02
High Sensitivity Ion-Selective Organic Electrochemical Transistor
Liang Li and Paddy K. L. Chan; Mechanical Engineering, The University of Hong Kong, Hong Kong, Hong Kong.

Ion signals play important roles in different kinds of biomedical processes. Traditionally, the detection methods usually require a relatively large sample size and expensive equipment to perform the ion concentration measurements. Here we proposed to use organic electrochemical transistors (OECTs) to measure the electrochemical signals from the ions. Comparing with the traditional methods, OECTs are conformal and flexible, more importantly, able to transfer to different objects to perform directly in-situ sensing. The OECT can also perform signal amplification function via transduce ion concentration signals to electrical signals. Here we develop the OECT based on the structure of gold source and drain contacts and ion-permeable conducting polymer Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) as channel. From the experimental results of different metal ions such as Ca\(^{2+}\), the ion sensitivity can be up to 2.5 times of the theoretical Nernst limit at a few hundred millivolts low-voltage operation. We also develop the ion-selective OECTs to detect the body fluid and we will fabricate this device on flexible substrate for future application in real-time ion signals detection. The
unique performance of our devices provide new opportunities in the field of implant biosensors for biomedical diagnostics.

EP06.06.03
Establishing a True Free-Standing Methodology for Characterizing Thin-Film Conjugated Polymer Mechanical Properties not Convoluted by Substrate Interactions Luke Gahanka, Kevin Ramos, Song Zhang and Xiaodan Gu; School of Polymer Science and Engineering, The University of Southern Mississippi, Hattiesburg, Mississippi, United States.

Conjugated polymers are showing ever increasing promise for both current and novel electronic applications. Much of the research for these materials has focused on optimizing electrical properties (such as OPV efficiency or electron mobility) at the detriment of understanding the mechanical properties which are necessary for device commercialization. One reason for this is that the active polymer layer is on the order of 100nm thick (or less) making direct mechanical characterization all but impossible. Our group has utilized the pseudo freestanding tensile test (film on water) to overcome this challenge enabling the calculation of parameters such as Young’s modulus and crack-onset-strain with minimal difficulty. This method has shown consistently lower modulus values than that obtained from buckling metrology. This may be due to a plasticization effect of the water, but the interaction of water with the thin film has not been sufficiently accounted for. Therefore, I will discuss a true free standing tensile test that provides direct mechanical characterization of conjugated polymeric thin films in air. This novel characterization technique was demonstrated on three polymer systems: polystyrene, poly(3-hexylthiophene-2,5-diyl), and polyfluorene at multiple film thicknesses to provide quantitative evidence of any measurable effect water induces in the pseudo freestanding tensile test. The film and bulk glass transition temperatures were measured via AC-chip calorimetry and DMA respectively. This enabled us to ascertain the effectiveness of this methodology across a broad range of dynamic systems. Furthermore, the free standing tensile test enabled in-situ characterization with darkfield microscopy under tensile strain thus providing further understanding in thin film deformation mechanics.

EP06.06.05
Vibrational Anharmonicity in Organic Semiconductors Maar Asher, Efrat Ramati, Boris Rybtchinski and Omer Yaffe; Weizmann Institute of Science, Rehovot, Israel.

Phonons in organic semiconductors are crucial for determining their charge transport properties. Current theoretical models treat these phonons within the harmonic approximation. These models fail many times to predict important electronic properties such as the charge-carrier mobility. Since organic solids have weak intermolecular interactions, the anharmonic components of their low-frequency vibrations are expected to be significant. We hypothesize that the reason for the failure to predict the electronic properties is the neglect of these anharmonic components.

I performed temperature-dependent low-frequency Raman measurements of oligo-acenes to quantify their anharmonicity. Results show a much stronger change in the peak position of the low-frequency modes with temperature compared to inorganic semiconductors. Analysis of these peak shifts shows strong anharmonic behavior - contributed from both thermal expansion and phonon-phonon interactions - likely to have a significant impact on electron-phonon interactions. Comparison of a series of oligo-acenes shows an inverse correlation between anharmonicity and intermolecular electronic coupling. I will also show photoluminescence and reflectance measurements to corroborate the connection between vibrational anharmonicity and the electronic properties of organic semiconductors.

EP06.06.06
Development of Novel Electrochromic Materials Based on Viologen-Conjugates Fengyu Su, Xiaowen Wu, Huan Ling, Yanjun Liu, Dan Luo, Xiaowei Sun and Yanqing Tian; Southern University of Science and Technology, Shenzhen, China.

Electrochromic (EC) materials and their correspondent EC devices (ECD) that change colors on application of voltages have attracted great research interests in the past several decades since they have commercial applications as smart windows, auto dimming rearview mirrors and static displays. Viologen has been widely investigated as an organic EC material since it has excellent redox properties accompanied with distinct color changes. However, most viologens only show color change from transparent or translucent yellow to blue. In order to make viologens more colorful, we designed and synthesized novel materials by inserting triphenyl moieties into bipyridine. These chromophores are expected to have abundant color changes. Further, these new viologen-conjugates possess phosphoric acid groups, which could help them anchor on the titanium dioxide (TiO$_2$) more firmly. A layer of nanostructured TiO$_2$ film (4.0 μm thick, TiO$_2$ particles are about 20 nm large) was coated on conducting F-doped tin oxide (FTO) glass, and the new viologen-conjugate was adsorbed onto TiO$_2$ particles by chemisorption. The films of new viologen-conjugate/TiO$_2$/FTO were characterized by using cyclic voltammetry. Color changes from transparent at 0 V to purple at -0.8 V and rust red at -1.1 V were observed. Next, Prussian blue (PB) was electrodeposited onto FTO glass and used as counter electrode. And then ECD was assembled by combining the working electrode of new viologen-conjugate/TiO$_2$/FTO, counter electrode of PB/FTO, and gel electrolyte. The ECD was characterized by using UV-vis spectrophotometer and electrochemical analysis system. The ECD showed a broad transmittance contrast over 60% at -2.5 V and -2.5 V.

Reference:

EP06.06.07
Direct Measurement of Single Molecule Charge Transport—From Molecular Design to Programmable Control Songsong Li, Hao Yu, Kenneth Schwieter, Bo Li, Jeffrey Moore and Charles Schroeder; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Programmable control of electron transport through organic semiconductors is a crucial step for designing integrated electronic devices for energy storage. Recent advances in molecular electronics have brought us closer towards achieving the ultimate limits in miniaturization and spatial and functional control over electronic performance. Despite recent progress, however, we still lack a full understanding of molecular-scale electron transport and how these properties are affected by chemical identity and sequence. In this work, we directly measure single molecule conductance using a scanning tunneling microscope-break junction (STM-BJ) technique. Oxazole-terminated molecules are found to exhibit interesting quantum interference phenomena through central phenyl rings and terminal oxazole rings, which can be used for controlling charge transport. In particular, the quantum interference of the central phenyl group follows a quantum circuit rule such that $G_{\text{central phenyl}} = 6$, whereas the c-type terminal oxazole ring shows constructive quantum interference. We can further precisely tune the conductance of oligophenyls via aromatic interaction with different background molecules. In this way, our work provides the fundamental electron and charge transport information to inform future programmable molecular electronics design.

EP06.06.08
Understanding the Molecular Origin of Polymorphic Transition via Nucleation and Cooperativity and Their Impact on Organic Semiconductors Hyunjoong Chung; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Understanding the molecular origin for better control of polymorphism is critical for the development of high performing, large area production of organic electronics. We explore a series of organic semiconductor systems with the same conjugated core and various bulky side chains to understand the polymorphic phase space. We demonstrate that substituting a bulkier silicon atom for a carbon atom in the side-chains compromises the packing environment such that they inhibit side chain rotation. We prove that either allowing, or preventing, the rotation of bulky sidechains triggers cooperative transition or nucleation and growth, respectively. We investigate the impact of both types of polymorphic transitions on electronic performance. By inducing nucleation and growth, we can access two kinetically stable polymorphs and study their electronic performance. From triggering cooperative transition, we have in situ access to different polymorphs with rapid reversible polymorphic transition for applications in next-generation smart multifunctional materials. This work offers a simple molecular design tool to access both polymorphic transition pathways and incorporate their advantages to organic semiconductors.

EP06.06.09
Tuning the Interfacial and Energetic Interactions Between a Photocexcited Conjugated Polymer and Open-Shell Small Molecules Daniel A. Wilcox, Jordan Snader; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.
Here, we demonstrate that Förster resonance energy transfer (FRET) is the dominant mechanism by which energy transfer occurs from a common conjugated polymer to various radical species using a combination of experimental and computational approaches. Specifically, we determined this by monitoring the fluorescence quenching of poly(3-hexylthiophene) (P3HT) in the presence of three radical species: (1) the galvinoxyl radical; (2) the 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxide-1-oxyl (PTIO) radical; and (3) the 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical. Both in solution and in the solid-state, the galvinoxyl and PTIO radicals showed fluorescence quenching that was on par with that of a common fullerene electron-accepting derivative, phenyl-C₆₁Bu, acridylic acid methyl ester (PCBM). This was due to the considerable overlap of their absorbance spectrum with the fluorescence spectrum of the P3HT species, which indicated that isoe energetic electronic transitions existed for both species. Conversely, TEMPO showed minimal quenching at similar concentrations in solution and at similar loadings in the solid state due to the lack of such an overlap. To support the determination of the mechanism, and to rule out photoinduced charge transfer, a potential competing process, pump-probe transient absorption measurements were employed. An increased rate of exciton decay in P3HT was observed when blended with the galvinoxyl radical and PTIO radical, consistent with an excited state transfer mechanism. Moreover, signals corresponding to the anion species of the quenchers were not observed, suggesting that charge transfer was not occurring at an appreciable rate for the compositions evaluated here. Additionally, computational studies suggested that FRET would occur at a significantly faster rate than photoinduced charge transfer. These computationally-predicted FRET rates were calculated from the spectral overlap of the P3HT fluorescence and the radical quencher absorbance spectra, while charge transfer rates were calculated by extracting Marcus theory parameters for the composite P3HT-quencher systems from density functional theory (DFT) calculations. Therefore, these computational results support the steady-state and time-resolved fluorescence experiments, and the results highlight the precise interactions between open-shell small molecules and closed-shell conjugated polymers in optoelectronic applications. Additionally, these findings suggest that long-range energy transfer can be accomplished in applications when radicals that can act as FRET acceptors are utilized, forming a new design paradigm for future optoelectronic applications.

EP06.06.10 Solution Process Feasible Highly Efficient Organic Light Emitting Diode with Hybrid Metal Oxide Based Hole Injection/Transport Layer Manveer R. Nagar, Rohit Ashok Kumar Yadav and Jwo-Huei Jou; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Solution-processable hybrid metal oxide (HMOS) active layers have attracted enormous attention because of their ease of fabrication and ability to provide a good balance of light-emitting and charge-transport properties. Organic light-emitting diodes (OLEDs) are fabricated with a combination of electron-injecting/transport layers (EIL), hole-injecting/transport layers (HIL), emissive layers (EML), and electron-transporting layers (ETL) that are used to control the injection, transport, and recombination of charge carriers. Conjugated polymer layers have often been used in OLEDs as they readily provide the necessary charge transport properties. However, in recent years, the use of inorganic materials as hole-injecting/transporting materials has gained importance due to their high energy levels and stability which may reduce device degradation over time. In this work, we present hybrid metal oxide (HMOS) layers that are solution-processable and provide a high electronegativity. The combination of the high electronegativity and high ionization potential with a suitable work function can serve as an excellent hole-injecting/transporting layer. In this work, we present one such hybrid metal oxide (HMOS) layer which we believe will be a great addition to the high energy level and solution-processible hybrid metal oxide layers.

EP06.06.11 Mean Free Path and Band Transport in Transistors Based on Polymer Semiconductors Xiao Wang and Ananth Dodabalapur, University of Texas at Austin, Austin, Texas, United States.

Semiconducting conjugated polymer thin film transistors (TFTs) with mobilities in the range of 0.1~20 cm²/Vs have been reported by many groups. This is a demand for higher mobility polymer TFTs; therefore, an accurate understanding of the physics of charge transport is necessary. However, a complete theoretical understanding and quantitative description of charge transport in such semiconductors has been difficult to attain. The mobilities and mean free paths are simply too low (on the order of intermolecular distance ~3 Å) for the application of conventional semiconductor transport theories. In this presentation, we will describe a very general solution based on the statistical nature of charge transport and introduction of a factor (mean free path factor) related to the probability of mean free path exceeding the minimum transport length. We are then able to apply the Boltzmann transport equation (BTE) with appropriate scattering mechanisms and obtain very good results that agree well with experiment[1]. This approach is very well suited to thin-film transistors based on polymer and organic semiconductors and also many amorphous oxide semiconductors with room temperature mobilities in the range 5~50 cm²/Vs[2]. We combine the mean free path factor, BTE solutions with an extended multiple trap and release (MTR) model that takes into account traps in the device to get an overall response. Several scattering mechanisms are considered based on the material properties. It is found that at low and intermediate temperatures, free carrier scattering by the trapped charge carriers is dominant. Carriers trapped in the semiconductor traps or at the semiconductor-dielectric interface can be considered immobile Coulomb scattering centers, and can scatter mobile carriers efficiently. At high temperatures, basically the room temperature (300K) or above, carrier-phonon scattering starts to dominate. An important phonon scattering mechanism in the semiconductor is the optical deformation potential scattering. Due to the structure of the conjugated polymers, the backbone generates low frequency optical phonons, and the optical deformation potential is fairly large in these soft model materials. This leads to very effective carrier scattering and decrease the mobility at high temperatures. Other scattering mechanisms including polar optical phonon scattering and acoustic phonon scattering are also considered into the evaluation of the band mobility for different temperatures and carrier concentrations. The resulting band mobility of conjugated polymers is in the range of 20~40 cm²/Vs, corresponding to 0.1~20 cm²/Vs for the effective MTR mobility in a TFT device. In the case of low carrier concentration, the carrier free path is assumed to approximately obey the Poisson distribution with occurrence number of zero (exponential distribution) and the mean free path factor. Thus, the mean free path of the carrier can be smaller than the intermolecular distance, there is still a fraction of free carriers that can survive travelling past that distance. This fraction of carriers is considered to participate the actual band transport. Thus, the apparent MTR mobility is further reduced by the factor of the mean free path survivor fraction. We compare results from our calculations with experimental data[1] for donor-acceptor polymers. The agreement is very good and attests the validity of our approach. Our work also points to clear directions that TFT device structures must possess for high performance.

Refs:
implementation of transparent composite electrodes in current heterojunction organic solar cells

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Recently transparent-composite-electrodes (TCEs) were introduced as a substitute for indium-tin-oxide (ITO) in bulk heterojunction organic solar cells (OSCs). In this study, an anode structure consisting of TiO2/Ag/TiO2 TCE with optimized layer thicknesses was implemented as an OSC to demonstrate its potential as a replacement for ITO. In addition, the compatibility of hole-transfer-layer (HTLs) of either MoO3 or poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were investigated in terms of their compatibility with the TCE. Corresponding control samples of ITO based OSCs were fabricated using PEDOT:PSS and MoO3 as the HTL. It is found that MoO3 HTLs benefited the OSC that utilizes a TCE as the anode. When using the MoO3 the as HTL, TCE based OSC has better performance than ITO-based OSC; and, it even rivalled the performance of conventional ITO-based OSC that utilizes PEDOT:PSS as the HTL. Outcomes of this study confirmed that even with the slightly lower transmittance in the visible portion of the light spectrum, TCEs did not degrade the light absorption in OSCs, and the efficiency of transporting photo-induced carriers in TCEs anodes was comparable or even better than ITO.

highly sensitive VOC sensor based on fluorinated isoindigo conjugated polymers

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With the increasing concerns for the environment and the progress in non-invasive diagnosis, monitoring volatile organic compounds (VOCs) have attracted considerable attention. Ammonia and acetone are of particular interest because they are related to chronic kidney disease and diabetes disorder, respectively. Multi-functional donor-acceptor conjugated polymers are potential candidates for building reliable ammonia and acetone sensors due to the recent advancement in the field of thin film transistor. In this report, we demonstrate that the transistor mobility, the device stability and the sensitivity of sensors can be greatly enhanced by incorporating functional groups directly on the polymer main chain. The fluorinated isoindigo polymers exhibit hole mobility with over an order improvement than their un-fluorinated counterparts. The novel polymer transistors sensor can discriminate various VOCs and detect 100 ppb ammonia gas and 50 ppb acetone gas within 2 min in air. This is the most sensitive polymer transistor-based sensor towards acetone ever reported. The influence of fluorination is systematically studied to understand the intermolecular interaction between the analytes and fluorine atoms. Exceptional sensitivity to ammonia is attributed to the hydrogen bond forming between fluorine and ammonia and the sensitivity to acetone is due to the change in the energy levels of frontier orbitals of the fluorinated conjugated polymers enhance the transistor and gas sensing performance, which is essential for building fast response and high sensitivity sensor platform.

dual gate transistors based on dual active layers

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Dual gate transistors based on rubrene/rubrene(p-p channels) and rubrene/DFH-4T(o-o-Diferrocenyl-quinquethiophene)(p-r channels) were fabricated. Traditional dual gate transistors using only one semiconductor active layer will inevitably result in bad injection in one channel. To maximize the charge injection area for both top and bottom channels, we adopted a staggered architecture with dual semiconductor layers. Gold source and electrodes are sandwiched between the bottom channel and the top channel. In the rubrene/rubrene dual channel dual gate OFETs, the average hole mobilities in the saturation regime for both bottom and top channel are around 5 cm2/Vs. The output characteristics for both channels exhibit good linearity in small Vg region, suggesting the charge injection is effective. Depending on the bias configuration, the threshold voltage of the bottom or top channel can be continuously modulated from 35.2 V to 45.6 V. In the rubrene/DFH-4T devices, the operating mode of the dual gate devices can be controlled as a p-channel, n-channel or ambipolar OFET. The AFM (Atomic force microscope) and XRD (X-ray diffraction) characterizations show that the growth of the top DFH-4T semiconductor is regulated by the bottom rubrene single crystals with distinct orientation. The dual gate transistors have the potential to be further constructed into inverters and complex logic circuits.

morphology stabilization using stamping transfer process via controlled PUA mold for perovskite and organic electronic devices

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Recently, stamping transfer process using by thin films or soft mold has been considered by advanced technology to overcome limits of wet coating such as spin or dip coating, which are composed of deposition of large area and specific region, the material loss, and penetration of solvents. Although the adhesion energy between stamp and targets was minimized for a successful transfer process, many researches have not discussed this factor. In this research, we introduced wetting coefficient related with the adhesion energy. We investigated the adhesion energy mainly depending on the surface energy of the stamp. We applied polyurethane acylate (PUA) as the stamp, of which the surface energy was modified to increase the transfer reproducibility. As a result, high-surface-energy PUA was used to form organic bulk hetero junction (BHJ) layer onto PEDOT:PSS/ITO substrates. The transferred device revealed a comparable efficiency, 95% relative to spin coating device. In order to decrease the fill factor of transferred device, we observed charge recombination and resistance through impedance spectroscopy.[1] Second, we applied stamping transfer to formation of inter-layer in planer-type perovskite photovoltaics. We have successfully fabricated the device with transferred inter-layer, 6,6-phenyl-C61 butyric acid methyl ester (PC71BM), onto perovskite layer by dry stamping transfer condition. The device exhibited enhanced Jsc and efficiency, which were caused by improved coverage of inter-layer on perovskite layer, correlated with increased electron mobility and exciton dissociation.[2] Finally, we fabricated organic photodetectors (OPDs) by stamping transfer process for photo sensitive BHJ layer. We confirmed a comparable performance of the transferred OPDs, compared to the device from spin coating. Especially, the dry transferred device exhibited superior durability (over 90%) for 350 hours to the spin coated device, because of morphology stabilization of photo sensitive layer, which led to suppression of degradation of the layer and burn-in loss.[3] This work provides a promising alternative process which can improve the device operation durability without burn-in loss by a simple and controllable transfer films.


W. Jing, D. H. Wang, ACS Appl. Mater. Interfaces, 10.1021/acsami.8b13375

Structuring polymer solutions upon liquid-vapor mass exchange

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Organic and hybrid thin film electronic devices, such as memory diodes, solar cells and transistors, typically contain a functional layer based on a blend of multiple polymeric or small-molecular species whose properties cooperatively give rise to a specific function. Depending on the desired functionality, phase separation during thin film solution processing is either encouraged or suppressed. Usually, at least one blend component is polymeric, so that mutual repulsion readily overcomes the entropic driving force to form stable mixtures. For this reason, it is often observed that during solution-casting droplet-like demixed morphology emerge due to (spontaneous) liquid-liquid (L-L) demixing. This presentation focuses on the role of this mode of phase separation in thin film electronics and how it is induced by mass exchange across the liquid-vapor boundary, i.e. solvent evaporation and vapor condensation. I give an overview on the work we have done to theoretically understand the influence of liquid-vapor exchange rates on demixing kinetics, as well as domain structure and composition. Multi-component continuum limit modeling demonstrates how microstructure and feature sizes emerge upon solvent evaporation and/or vapor condensation. The numerical simulations yield morphologies consistent with experimentally observed structures and demonstrate how domain size and phase composition are affected by internal and environmental factors.

Dodecaborane Clusters as Novel Tunable Dopants for Conjugated Polymers

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Doping conjugated polymers is an effective way to tune their electronic properties for thin-film electronics applications. Chemical doping of semiconducting polymers involves the introduction of a strong electron acceptor or donor molecule that can undergo charge transfer (CT) with the polymer. The CT reaction creates electrical carriers on the polymer
chain while the dopant molecules remain in the film as countereions. To dope polymer films, we employ a sequential process (SqP) in which a pure polymer layer is deposited first, followed by infiltration of the dopant in a second step using a semi-orthogonal solvent. SqP overcomes the problems typically incurred by blend-doping, where the polymer and dopant are mixed in solution, which results in aggregation at high concentration. The exceptional film quality achievable with our SqP doping method allows us to employ electrical measurements over macroscopic length scales, such as Van der Pauw conductivity measurements as well as AC Hall effect and impedance measurements of carrier mobility.

This work focuses on the use of substituted icosahedral dodecaborane (DDB) clusters of the form $\text{B}_2\text{O}_2\text{R}_2$ as a new class of dopant molecules, where $\text{R}$ is a substituted benzyl group. The redox potentials of DDBs can be rationally tuned via modification of the R-group substituents without a significant change to the size or shape of the dopant molecule. These tunable dopants provide a unique handle on the energetic offset that governs the driving force for doping via integer CT. Here, we disentangle the effects of energetic offset on the production of free and trapped carriers in DDB-doped poly-3-hexylthiophene (P3HT) films.

In DDB-doped P3HT films, in general, we find that conductivity and polaron absorption amplitude increase with increasing reduction potential, yielding conductivities on the order of 12 Scm. Since DDBs tend to localize electron density on their core, we have shown that the bulky corona of substituents on the clusters provide spatial isolation of the corona. The polaron is therefore Coulombically shielded from the corona, thereby reducing electrostatic interactions, resulting in highly delocalized and mobile carriers with mobilities up to 0.1 cm$^2$/Vs and effective conductivities up to 32 S/cm even in very non-crystalline polymer films. In these films, nearly all carriers are free, whereas it has been shown that the core of substituted compounds like FATCNO trap 95% of carriers, due to their small size and non-crystalline properties of the corona. Given the high conductivity but distinct loss off crystallinity observed, we explore the properties of these DDB-doped films as potential thermoelectric materials. The low crystallinities should lead to low thermal conductivities, even while the electrical conductivity is maintained, allowing optimization of the thermoelectric figure of merit.

**EP06.06.18**

**Amphiphilic Conjugated Polymers for Nanoparticle Stabilization**

Sonam Saxena, Philipp Meier, Alexander Colsmann, Wallace W. Wong, and David J. Jones.

Solution-processable semiconducting materials in organic solar cells (OSCs) enable the roll-to-roll printing of functional devices. However, the dissolution of these materials commonly requires toxic solvents, thus hindering the translation to industry. To enable large scale printing in industry, they should be formulated as inks using a less toxic medium such as alcohol or even water.

Researchers have fabricated OSCs by dispersing semiconducting materials in water/alcohol with the help of surfactants. However, significant surfactants remained in the active layer even after extensive dialysis, reducing the device performance and solar cell life-time. Recently, devices were fabricated using a dispersion of poly-3-hexylthiophene (P3HT) with iodine-C$_6$Br$_2$ (ICBA) in methanol and showed a 3.8% device efficiency without the need of a surfactant. However, in this case, the performance was highly dependent on the degree of polymer used for dispersion. Herein, we show the requirement of an appropriate surfactant which not only controls the size of nanoparticles but also increases nanoparticle stability whilst maintaining device efficiency.

To address this problem, we synthesized P3HT end-capped with pyridine. We expected this pyridine-P3HT to be protonated on addition of acid and act as a surfactant by making an electrical double layer around the nanoparticles, inducing a repulsive interaction and preventing aggregation, however under thermal annealing the pyridinium salt would decompose removing all trace of the acid. By using a combination of 1.5 w% pyridine-P3HT and trifluoroacetic acid as additives, stable P3HT:ICBA nanoparticle dispersions of up to 30 mg/mL in methanol were achieved. The nanoparticles in these dispersions were 120 ± 5 nm, and the dispersions were stable up to 60 days. Inverted architecture OSC built using these nanoparticle dispersions exhibited 3.4% efficiency, a result that is comparable to the state-of-the-art P3HT:ICBA solar cells fabricated under optimized conditions using chlorinated solvents.

**EP06.06.19**

**Vertical Organic Charge Modulated FET Devices for Sensing Applications**

Andrea Spanu, Laura Martinez, Annalisa Bonfiglio, and Piero Cosseddu.

Since the discovery of the first conductive polymer, organic electronics helped disclosing a whole new world of possibilities in the realization of, among several other applications, flexible displays, mechanically compliant (but also implantable and bioreosorbable) sensors and biosensors, and tactile sensors for next generation artificial skin applications.

Despite these remarkable achievements and more than 5 decades of technical advancements, the field of application of organic electronic devices is still relatively narrow, due to the intrinsic properties of the semiconductive materials usually employed. In particular, common limitations are the low switching speed caused by the intrinsic low mobility of the charge carriers within the most common polymers and small molecules used (this limitation preventing most of the organic transistor to be used as reference devices), and the limited devices resolution, the latter issue being mainly due to the difficulty of fabricating short channel transistors while at the same time using low-cost and large area fabrication techniques.

In order to overcome these apparently unavoidable issues, during the last 15 years a new type of organic transistor has been introduced, namely the vertical organic transistor (vOFET). This peculiar “vertical approach” allows to obtain short channels without the need of expensive fabrication techniques, thus representing a very interesting technological advancement with respect to pre-existing OFETs. In this work we report about a novel and easy approach to the realization of vertical organic transistors that includes the use of Parylene C as both the “core” of the vertical structure and the gate insulator. The fabrication process has been optimized in order to have the possibility to obtain highly flexible and ultra-conformable transistors, being such devices fabricated on micrometer-thick films (either Parylene C or polyamide-imide) that, after the device fabrication, can be conveniently detached from the carrier substrate allowing it to be transferred onto whatever kind of surface. Moreover, we will also demonstrate that such approach is particularly suitable for the fabrication of sensing devices. In particular, we employed a double-gated organic transistor called organic charge modulated FET (OCMFET), which has established itself during the past 10 years as a versatile sensor with an ultra-high sensitivity.

The combination of the proposed novel and convenient approach to the fabrication of vertical organic transistors (with the possibility of realizing high-resolution and faster switching devices) and the remarkable features of the OCMFET represents an interesting advancement within the organic electronics scenario, in that it will allow to obtain reference-less, ultra-sensitive sensors arranged in conformable high-density arrays, while keeping the process low-cost, thus offering considerable advantages to the field of organic sensing and biosensing.

**EP06.06.20**

**Substituents Engineered Deep-Red to Near-Infrared Phosphorescence from tris-Heteroleptic Iridium(III) Complexes for Solution Processable Red-NIR Organic Light-Emitting Diodes**

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Research on near-infrared- (NIR-) emitting materials and devices has been propelled by fundamental and practical application demands surrounding information-secured devices and night-vision displays to phototherapy and civilian medical diagnostics. However, the development of stable, highly efficient, low-cost NIR-emitting luminophores is still a formidable challenge owing to the vulnerability of the small emissive bandgap toward several nonradiative decay pathways, including the overlapping of ground- and excited-state vibrational energies and high-frequency oscillators. Suitable structural designs are mandatory for producing an intense NIR emission. Herein, we developed a series of deep-red to NIR emissive iridium(III) complexes (Ir1–Ir4) to explore the effects of electron-donating and electronwithdrawing substituents anchored on the quinoline moiety of (benz[b]thiophen-2-yl)quinoline cyclometatating ligands. These substituents help engineer the emission bandgap systematically from the deep-red to the NIR region while altering the emission efficiencies drastically. Single-crystal X-ray structures authenticated the exact coordination geometry and intermolecular interactions in these new compounds. We also performed an in-depth and comparative photophysical study in the solution, neat powder, doped polymer film, and freeze matrix at 77 K states to investigate the effects of substitution on the excited-state properties. These studies were conducted in conjunction with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Most importantly, the –CH$_3$ substituted Ir1, unsubstituted Ir2, and –CF$_3$ substituted complex (Ir4) were promising novel compounds with bright phosphorescence quantum efficiency in doped polymer films. Using these novel molecules, deep-red to NIR emissive organic light-emitting diodes (OLEDs) were fabricated using a solution-processable method. The unoptimized device exhibited maximum external quantum efficiency (EQE) values of 2.05% and 2.11% for Ir1 and Ir2, respectively.
Emission Gain Narrowing in Organic Semiconductor Single Crystal

Minji Kang, Yeong-A Kim, In-Bok Kim, Dongseong Yang, Yeonsu Choi and Dong-Yu Kim; School of Materials Science and Engineering (SMSE), Gwangju Institute of Science and Technology, Gwangju, Republic of Korea; Department of Mechanical and Aerospace Engineering, University of Missouri-Columbia, Columbia, Missouri, United States; Department of Solid State and Structural Chemistry, Tsinghua University, Shenzhen, China. Inorganic materials with high mechanical flexibility, lightweight, and solution processability are highly desirable as organic electronic devices. We report an inorganic-organic hybrid material, 

Emission Gain Narrowing in Organic Semiconductor Single Crystal

EP06.06.22

Influence of the Mobility Ratio and Energetics of n-Conjugated Polymers on the Thermoelectric Properties of Polymer Blends

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Conjugated polymers can be used in mechanically flexible and low cost thermoelectric (TE) devices, but their thermoelectric performance must be improved to make them commercially viable. The performance of thermoelectric materials depends on the electrical conductivity, Seebeck coefficient and thermal conductivity. In polymer based TE materials the polymer needs to be doped to become electrically conductive. The higher the doping concentration, the more electrically conductive the material becomes, but generally at the cost of a decrease in the Seebeck coefficient. Blending of n-conjugated polymers has been proposed as a method to minimize the tradeoff between electrical conductivity and the Seebeck coefficient, thus potentially allowing higher power factors to be reached. By blending two polymers, the total density of states (D.O.S.) will be manipulated, which may be used to alter the energy dependence of charge transport in the TE material. The major parameters that we expect to impact the power factor in polymer blends are the mobility ratios between the two pure polymers and the shape of the D.O.S. (i.e., the disorder and the energy offsets between the D.O.S. distributions of each polymer). Here, we modified a model introduced by Bässler and Arkhipov to theoretically probe how these two parameters impact thermoelectric performance. These calculations are then used to fit experimental data of various polymer blends with varying mobility ratios and D.O.S. distributions. We find that adding a polymer with a narrower D.O.S. and higher mobility with respect to host polymer can lead to an enhancement in the power factor.

EP06.06.23

Donor-Acceptor Copolymers and Sol-Gel Processable ZnO for Hybrid Photodetectors and Thin-Film Transistors

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Hybrid organic-inorganic semiconductor interfaces have attracted attention in photodiodes and field-effect transistors (FETs) due to the realization of intrinsic p-n junctions and their mechanical flexibility. Organic copolymers based on diketopyrrolopyrrole (DPP) cores have also gained significant interest for application in FETs because of their high p-type carrier mobilities as well as high power conversion efficiencies in solar cell structures. In addition, grazing-incidence x-ray diffraction (GIXRD) reveals crystalline stability of phenoxy-capped DPP-based monomers [1]. With the difficulty of developing high-mobility n-type organic semiconductors [2] due to the necessity of low LUMO levels and ambient environment stability, solution processable inorganic materials are an excellent alternative. ZnO is an intrinsic n-type semiconductor which is non-toxic and sol-gel processable, creating avenues for film patterning [2] and fully solution processed devices. These ZnO films are also able to be easily treated, reducing lattice defects through UV-Ozone processing. This decreases the dark current and increases responsivity in hybrid photodetectors and yields improved electrical performance in FETs. Additionally, cross-sectional electron microscopy techniques reveal hidden characteristics within the morphologies of the films and provide insight as to how processing conditions impact FET and photodiode operation.

We support the acknowledgement of this work through the National Science Foundation under Grant No. ECCS- 1707588


EP06.06.24

A Theoretical Study of Two Functional Derivatives to Unsymmetrical Squaraine Donors for Organic Photovoltaics from First-Principle Simulation

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Organic photovoltaic (OPV) cells have drawn increasing attention for decades due to the advantages of low cost, flexiblity, lightweight, solution processability, and potential applications in large area devices. The development of new materials, nanomorphological control and device design has led to significantly improved solar cell efficiency up to 15% up to now. Over the long journey of three decades, many photoactive dyes have been systematically explored in metal/electrode/dye/transparent oxide electrode (typical PV structural planarity arising from a double bond linkage between aromatic rings. Despite the merits as conjugated moiety, the incorporation of the quinoidal platform into the conjugated molecules based on quinoidal structure. The quinoidal structure has been considered as a promising building block to achieve efficient charge transport due to their high low-cost and flexible electronics. The structure-property relationship of novel organic semiconducting materials has been explored with the development of device engineering technique leading to understanding charge transport mechanism and device physics. In this work, we have focused on the investigation of structure-property relationship of conjugated molecules based on quinoidal structure. The quinoidal structure has been considered as a promising building block to achieve efficient charge transport due to their high structural planarity arising from a double bond linkage between aromatic rings. Despite the merits as conjugated moiety, the incorporation of the quinoidal platform into the

EP06.06.25

Novel Quinoidal Conjugated Molecules and Polymers for High Performance Organic Field-Effect Transistors

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Organic field-effect transistors (OFETs) based on organic semiconductor materials have intensive interest both in the academic and industrial fields because of their application in low-cost and flexible electronics. The structure-property relationship of novel organic semiconductor materials has been explored with the development of device engineering technique leading to understanding charge transport mechanism and device physics. In this work, we have focused on the investigation of structure-property relationship of conjugated molecules based on quinoidal structure. The quinoidal structure has been considered as a promising building block to achieve efficient charge transport due to their high structural planarity arising from a double bond linkage between aromatic rings. Despite the merits as conjugated moiety, the incorporation of the quinoidal platform into the
conjugated polymer backbones has suffered synthetic difficulty. Here, some derivatives of quinoidal small molecules and polymers with various quinoidal platforms were synthesized, and their structure-property relationships was investigated. Moreover, field-effect transistors based on these compounds were fabricated and characterized about electrical properties. Among them, OFETs based on poly(quinoidal thiophene-bithiophene) (PQuT-BT) prepared by off-center spin coating showed the unprecedented highest hole mobility of 8.09 cm²/V·s among reported quinoidal polymers. Furthermore, we fabricated OFET devices based on this polymer via printing methods applying unidirectional shear forces leading to high molecular alignment and device uniformity in large area.


EP06.06.26
Flexible Transparent Electrodes via Printed Polymer-Sphere Networks for Polymer Photodiode and Light-Emitting Diode
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Flexible transparent electrodes have drawn increasing interest due to the rapid development of flexible electronics and sensors. Metal networks is an emerging novel transparent electrode, which has shown potential applications in organic electronics and wearable sensors. However, the techniques which can realize facile fabrication of non-transfer, large-area and low-roughness metal-network are desperately desired. Our work demonstrates a print-compatible method for fully interconnected metal networks directly on the flexible substrate. A patterned high-k dielectric substrate and then convert photolithography into polymer networks. We combine evaporation processes to transfer the networks into interconnected metal structures on the substrate. We demonstrate such transparent electrodes as the top electrodes both in the spin-coat and printed polymer photodiode and light emitting diode. This technique is low-cost, print compatible and can achieve the low-roughness and large-area transparent electrodes directly on the flexible substrate, which shows potential applications in large-area organic electronics.

EP06.06.27
Dynamic Composition of Electrolyte Gated Organic Mixed Ionic Electronic Conductors
Bryan D. Paulsen, Vishak Venkatraman and Jonathan Rivnay; Biomedical Engineering, Northwestern University, Evanston, Illinois, United States.

Organic mixed ionic electronic conductors (OMIECs) are semiconducting polymers able to efficiently transport both ionic and electronic charge, and efficiently transduce ionic and electronic currents. This has led to their success as the channel materials in organic electrochemical transistors (OECTs) for biological sensing applications. By using an experimentally verified TCAD model developed in Silvaco Atlas for the high mobility polymer semiconductor, PDPP-TNT, we show how optimizing the patterning of patterned TFTs, which are defined as narrow semiconductor stripes atop a gate dielectric with air or a low permittivity dielectric between each stripe. A nanostripe TFT device will focus on the latter two sources of nanostripe enhancement since they are more broadly applied to all disordered semiconductor systems.

EP06.06.28
Nanostripe Channel Patterning of Polymer Thin-Film Transistors for Improved Performance
Kelly Liang, Oleksiy O. Krutko and Ananth Dodabalapur; Microelectronics Research Center, The University of Texas at Austin, Austin, Texas, United States.

In recent years, researchers have explored various methods of shaping the active semiconductor layer to improve thin film transistor (TFT) performance. The shaping has varied in methods and architectures from micron scale etched stripes for amorphous metal oxides, to hundreds of nanometers wide printed polymer stripes, and also to textured or grooved substrates for various materials including organics and polymers. It has been reported by these and other works that patterning can improve performance of polymers and it has been observed that patterning improves key transistor characteristic across many TFT material systems. We present a detailed analysis of the electronic origins of improvements seen by nanopatterning devices and a means to optimize TFT device design to enhance these improvements. Our work specifically focuses on the unique advantages of nanostripe patterned TFTs, which are defined as narrow semiconductor stripes atop a gate dielectric with air or a low permittivity dielectric between each stripe. A nanostripe TFT device features multiple strips with a common gate and common source and drain contacts.

There are three main origins of nanostripe enhancement—first is improved morphological order of the disordered materials especially polymers, as previously reported by several groups; second is greatly enhanced induced carrier densities which is especially advantageous for disordered semiconductors which display carrier mobilities that are approximately linearly dependent on carrier concentration; third is improved gate control, similar to FinFET schemes seen in silicon and other semiconductor transistors. With the combined effects of all three, nanostripe devices can expect substantially improved drive currents and gate control over their unpatterened thin-film counterparts. This presentation will focus on the latter two sources of nanostripe enhancement since they are more broadly applied to all disordered semiconductor systems. By using an experimentally verified TCAD model developed in Silvaco Atlas for the high mobility polymer semiconductor, PDPP-TNT, we show how optimizing the patterning of TFTs into nanostrips maximizes enhancement of foundational transistor performance metrics, such as increased carrier mobility, lower of off-current, reduced threshold voltage, and improved subthreshold swing. By adjusting the geometry of the nanostripe—we namely by finding the optimum stripe width and stripe pitch, and making no adjustments to any other material parameters, we show that the drive current can be improved by a factor of 13. The nanostripe geometry focuses electric fields along the edges of stripe, maximizing trap state filling in those areas, to greatly improve carrier transport. While similar effects are seen in nanogroove and FinFET structures, nanostrips (which sit atop the dielectric) generate the most local enhancement. Further experimentation is underway to improve the accuracy of the TCAD model.


EP06.06.30
Raman Crystallography as a Probe of Phonon-Mediated Anisotropic Carrier Mobility in Single Crystal Organic Semiconductors
Adam Biachesi1, Emily Bittle1, Lisa Freni1,2, Andrew Herzing1, Thomas Allisson1, David Gundlach1 and Angela Hight Walker1; (National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 1Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, United States.

Understanding charge transport in organic semiconductor materials is an important step in the development of high-performance electronics employing these materials. Intermolecular motions are postulated to limit carrier mobility in organic electronics due to the formation of transient charge carrier localization, which prevents band-like transport. Raman spectroscopy is a powerful technique to nondestructively investigate such vibrational modes of organic crystals. These phonons are spatially localized within the lattice and correlate to the underlying crystallographic structure of the material. This provides a straightforward means to investigate the crystallinity, orientation, composition, and phase with high spatial resolution and no sample preparation. Here we present a polarization-orientation Raman spectroscopy analysis of single-crystalline organic semiconductor tetracene. We find five distinct vibrational modes in the low-energy regime (~25 meV) that are ascribed to intermolecular lattice phonons. Polar plots indicate that these motions are characterized in agreement with group theory, directed within the ab plane of single-crystalline tetracene (001), as confirmed by electron diffraction. We then correlate the geometry of these phonon modes with the anisotropic field-effect mobility found within this plane and utilize density functional theory modeling of the corresponding molecular motions to examine the potential impact of orbital overlap between molecules on carrier transport. Collectively, these data suggest that transient localization due to Raman-active intermolecular motion has directionality within the single-crystalline structure of tetracene molecules and, more generally, the lattice motion strongly influences the inherent charge transport behavior and anisotropic character of organic semiconductors.

EP06.06.33
Controlling Doping in Semiconducting Polymers has significantly reduced dark current (~1 × 10⁻³ A/cm²). Organic semiconductors have very low mobility (e.g., 10⁻⁵ cm²/Vs) and a short free mean path [2]. This addresses the challenge of improving conversion efficiency by incorporating highly anisotropic carbon nanomaterials (CNMs) such as carbon nanotubes (CNTs) and/or graphene nanoplatelets (GNPs), which have been shown to improve charge transport towards the electrodes. Although CNMs have been used before in OPVs, the focus of our research is to elucidate the effect of the structural properties of the CNMs on OPV performance. More specifically, we address the issue of improving the performance of a new hybrid OPV device by combining the physical and chemical characteristics of light-sensitive conjugated polymers (CP), e.g. P3HT, with the high electrical conductivity of the CNMs in a composite photoactive layer. Special care is taken to control the optoelectronic properties and PV characteristics of the hybrid OPV through the morphology of the CNMs and to study the improvement of the exciton dissociation efficiency of the CNMs/photosensitive polymer interface, in a planar heterojunction photovoltaics configuration. The obtained results show photoconversion efficiencies of about 3.85 % and 4.05 % for CNTs and GNP loads of 0.5 and 0.8 wt. %, respectively. The main parameters will be presented and an outlook into the future will be discussed accordingly.

### References


[2] Deepak Kumar Dubey and Jwo-Huei Jou; National Tsing Hua University, Hsinchu, Taiwan.

#### EP06.06.34

**Infrared-to-Visible Up-Conversion OLEDs Using Novel Infrared-Sensitive Low-Bandgap Organic Donors and/or Acceptors**

Vishall Yeddu, Gijun Seo, Hyocheol Jung and De Young Kim; Oklahoma State University, Tulsa, Oklahoma, United States.

Infrared (IR)-to-visible up-conversion organic light-emitting diodes (OLEDs) using various novel low-bandgap organic donors and/or acceptors as the organic IR sensitizing layer were fabricated with an IR sensitivity beyond 1 μm. The novel donors and acceptors have narrow bandgaps of 0.9 – 1.2 eV and showed strong absorption in the visible as well as IR region till 1200nm. IR photodetectors are first fabricated to evaluate the new donors and acceptors as the IR sensitizers in the IR-to-visible up-conversion OLEDs. The multi-layered photodiode structures with an electron blocking layer (EBL) and a hole blocking layer (HBL) are used to reduce its dark current, thus resulting in high detection. Most of photodetectors with novel IR sensitizers showed strong IR sensitivity in the near-IR wavelengths from 700 nm to 1200 nm. The photodetectors with novel IR sensitizers showed detectivities higher than 10¹¹ Jones in the multi-spectral region (300-1100nm) and the maximum detectivity of 3.0 × 10¹² Jones at the wavelength of 800 nm due to significantly reducing dark current (~1 × 10⁻⁴ A/cm² at 0.1V). Using this novel low-bandgap organic materials as the IR sensitizer, IR-to-visible up-conversion OLEDs were fabricated with an IR sensitivity up to 1,200 nm. The IR up-conversion OLED successfully converted invisible near-IR light of 700nm-1200nm directly to visible green light with a peak emission wavelength of 520 nm. This is the very first report of all-organic IR-to-visible up-conversion OLED with near-IR sensitivity beyond 1100 nm which Si-based photodetectors cannot offer.

#### EP06.06.35

**Highly-Efficient Solution-Processed Organic Light Emitting Diodes with Blend V:O-PEDOT:PSS Hole-Injection/Hole-Transport Layer**

Rohit Ashok Kumar Yadav, Deepak Kumar Dubey and Jwo-Huei Jou; National Tsing Hua University, Hsinchu, Taiwan.

Organic light-emitting diodes (OLEDs) have attracted huge demand because of their intrinsic characteristics and ability to reach the pinnacle in the field of high-quality flat-panel displays and energy-efficient solid-state lighting. High-efficiency is always a key crux for OLED devices being energy-saving and longer life-span. OLEDs have encountered enormous difficulties in meeting the requirements for large-sized devices due to a major limitation in vacuum thermal evaporation technology. In multi-layered OLED devices, the quantity of the charge injection/transport layer is a crucial factor for the operating-voltage, power-efficiency, and stability of the device. Transition metal oxides have shown great potential owing to their wide range of possible energy level alignments, balanced charge injection, and improvement of carrier mobilities. In this study, we report an efficient low-driving solution processed OLED devices composed of blend V:O-PEDOT:PSS hole-injection/hole-transport layer (HIL/HTL). The electroluminescent characteristics of blend V:O-PEDOT:PSS based devices were studied with the structure ITO/PEDOT:PSS or V:O-PEDOT:PSS:MT-DATA:Ir(2-phenyl)/TPBi/LiF/Al. The V:O-PEDOT:PSS based OLEDs exhibited relatively high device performance and low roll-off than that of the counterpart PEDOT:PSS devices in terms of a maximum luminance of 17,670 cd/m², power-efficiency of 15.7 lm/W, external quantum efficiency of 7.7%, and more importantly low turn-on voltage of 2.2 V. The fabricated device exhibits high color stability, lifetime, and excellent saturation compared to counter devices. These are the highest power efficiencies ever reported for this particular device architecture with blend transition metal oxide-organic complex.
novel concept based on an organic electrochemical transistor and show how these challenges in the field such as state-retention and linear conduction tuning can be overcome. We investigate chemical doping of the active organic semiconductor material with additive amines for improved oxidation state stability over a large range and enhanced device-to-device variability, an essential characteristic for efficient large-scale arrays. Finally, we demonstrate that this device can be entirely fabricated on flexible substrates, introducing neuromorphic computing to large-area flexible electronics and opening up possibilities in brain-machine interfacing and adaptive learning of artificial organs.

1 van de Burgt et al. Nature Electronics, 2018
2 van de Burgt et al. Nature Materials, 2017
3 Keene et al. J Phys D, 2018

8:45 AM EP06.07.03
Doping Organic Semiconductors for Thin-Film Transistors Julianna Panidi1, Jaspreet Kainth1, Alexandra Paterson2, Martyn McLaughlan1, Martin Heeney4 and Thomas D. Anthopoulos2, 1Department of Physics, Imperial College London, London, United Kingdom; 2KAUST Solar Centre, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 3Department of Materials, Imperial College London, London, United Kingdom; 4Department of Chemistry, Imperial College London, London, United Kingdom.

Improving the performance and reliability of organic electronic devices is necessary for their successful commercialization. New materials combined with improved synthetic routes have so far lead the way to the development of state-of-the-art organic electronic devices and their application in a range of emerging forms of electronics. An alternative and less studied approach towards high performing organic semiconductors (OSC) is the use of molecular dopants as a mean for tuning their physical properties and often the resulting device characteristics. In organic thin film transistors (OTFTs) doping results to improved charge carrier mobility, by eliminating the threshold voltage while reducing parasitic contact resistance. Although highly useful, detailed understanding of the doping mechanism still remains challenging, with the most understood process being that of the integer charge transfer. The key requirement for doping to occur is the minimum energy offset between the dopant and the host material. In the case of n-type materials the dopant has to donate an electron from its highest unoccupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the host. Although numerous studies have been reported on p-type doping of organic semiconductors, work on molecular n-doping remains surprisingly limited. The main reason for this is the difficulty of identifying suitable dopants that are stable and efficient.

Here, we report the use of a new molecular dopant that is able to n-dope a number of organic semiconductors, which are then used as the channel materials in OTFTs. We show that key transistor parameters such as charge carrier mobility, contact resistance and threshold voltage improve dramatically upon addition of the dopant. The doping effect was studied using different methods including Electron Paramagnetic Resonance (EPR) and temperature dependent field-effect electron transport measurements. The impact of the dopant on the morphology of the OSCs has also been studied using Atomic Force Microscopy (AFM) and X-Ray diffraction (XRD) measurements, yielding interesting insights on the impact of doping on the layer microstructure for the first time. Overall, this work highlights that controlled doping of organic semiconductor materials is the key for improving the electronic characteristics of n-channel OTFTs.

9:00 AM EP06.07.04
Ohmic Charge Injection and Low-Power OFETs Achieved by Organic Semiconductor Monolayer Crystals Boyoi Peng and Paddy K. L. Chan; Hong Kong University, Hong Kong, China.

In organic thin-film transistors (OTFTs), the charge accumulation region is within several nm away from dielectric interface. For the monolayer crystals of small-molecule organic semiconductor materials, all the molecules contribute in forming the conductive channel and receive benefits from long-range in-plane ordering. A meniscus-guided solution-processing method is employed to grow monolayer crystals of C49-DNTT with single-crystalline domain size as large as millimeters. Intrinsic field-effect mobility of >12 cm²/V·s is achieved. More importantly, the ultrathin thickness minimizes the charge injection barrier for the top-contact electrodes, allowing an ohmic hole injection and a low contact resistance (Rc, W) of 67±15 ohm cm. The low contact resistance ensures low voltage drops at the metal/semiconductor interface, allowing the device to operate even at VDS = ~1 mV. It opens a new direction of low-power OFET that operates at pico-watts, which can only be achieved by high-mobility short-channel OFETs with very low contact resistance. The physics origin of forming such low contact resistance of OFETs will also be discussed.

9:15 AM EP06.07.05
Molecular Surface Chemistry for Improved Interfaces in Organic Electronics Jonathan Hopwood1, Jixin Chen2 and Jacob Ciszek1; 1Loyola University Chicago, Chicago, Illinois, United States; 2Chemistry, Ohio University, Athens, Ohio, United States.

Organic optoelectronic devices (OLED, OFETs, etc.) contain at least one, if not multiple instances of overlayers deposited onto organic semiconductors. The generated interface is inherently flawed with issues such as non-ohmic contact, overlayers delamination, or deposition induced damage arising. Traditionally, this is addressed by physical vapor deposition of yet another layer or by reengineering the materials in the device stack. In contrast, a reaction based approach allows for a wider range of function to be installed via molecular components in an organized and oriented manner, while all take advantage the inherent reactivity of the organic molecules which comprise the semiconducting layer. We have developed this approach via a “click-like” Diels-Alder chemistry whereby prototypical acene films (tetracene or pentacene) can be appended with a variety of small molecules to form an interfacial layer only ~5 Å thick. This chemistry is then applied towards improving the metal on semiconductor contact. As a demonstration of principle, Diels-Alder chemistry is utilized to form covalent bonds linking the organic semiconductor with a deposited metal contact thereby eliminating the poor adhesion present in this system. Application of the chemistry towards contact potential shifts is presented, while works towards sensing applications concludes the talk.

9:30 AM EP06.07.06
Individual Contributions of the Source and Drain Contacts to the Total Resistance in Organic Thin-Film Transistors Investigated Using Kelvin Probe Force Microscopy (KPFM) Melanie Brouillard1, 2, Nicolas B. Bercu1, Olivier Simonetti1, Hagen Klauk1 and Louis Giraudet1, 1Université de Reims Champagne-Ardenne, Reims, France; 2Organic Electronics, Max Planck Institute for Solid State Research, Stuttgart, Germany.

An important requirement for organic thin-film transistors (OTFTs) is a reproducibly small and well-controlled contact resistance. A popular method for determining the contact resistance is the transmission line method (TLM), which has the drawback that it is valid only under the assumption that the contact resistance is linear, which is generally not the case. Another drawback is that TLM cannot differentiate between the source resistance (RS) and the drain resistance (RD). Using surface potentiometry on operating OTFTs [1], resistances at the source and drain contacts can be measured independently from the potential drops measured in the transistor channel. We have carried out KPFM measurements on OTFTs with different doping methods [2.3.4,5] and n-type semiconductors [6] fabricated in the bottom-gate, bottom-contact (inverted coplanar) configuration. A 10-nm-thick layer of aluminum oxide deposited by atomic layer deposition was used as the gate dielectric, and gold was used for the source and drain contacts. In some of these OTFTs, the bias sequences applied during the KPFM measurements induced changes of the contact behavior, and in some cases the current-voltage characteristics of the contacts became nonlinear. On these TFTs, potential drops (UI(stray)) were observed on the KPFM profiles both at the source and at the drain contacts. From the simultaneous measurement of the drain current (Id), the contact characteristics (Id/I(U(stray))) relationship were obtained. When the Id/I(U(stray)) relationship is linear, the contact resistance can be obtained from this relationship. In some of the TFTs examined here, the current-voltage characteristics of the source and drain contacts are nonlinear, following a power law with an exponent between 1.5 and 3. In this case, we were able to estimate the contact resistance only to within an order of magnitude. Also, the potential drop at the source contact appears to be significantly larger than the potential drop at the drain contact, as one would expect from a contact exhibiting a large misalignment of the energy levels. To understand how each contact contributes to the total contact resistance, similar measurements were performed at various gate-source voltages. In addition, the measurements were repeated to observe the evolution of the contact characteristics with time.

References

9:45 AM BREAK

10:15 AM EP06.07.07
Recent advances in bioelectronics are making the gap between electronic systems and human body ever closer. Despite these recent successes, the majority of bioelectronic devices still rely on electrode materials which are physically and mechanically dissimilar to biological tissues. Biological tissue is soft and contains large amounts of water with dissolved ionic species. In contrast, most inorganic materials and dry polymers in bioelectronic devices exhibit much higher elastic moduli with virtually no water content. Among many engineering materials, hydrogels show a great promise as ideal interfacing materials to biological tissues, owing to their unique tissue-like mechanical property, water-rich nature, superior biocompatibility, and ease in engineering. However, conventional hydrogels typically lack electronic conductivity, and the ionic conductivity of hydrogels in physiological conditions is very low. Unlike conventional hydrogels, conducting polymer hydrogels uniquely offer both electronic and ionic conductivity, and have been extensively explored for bioelectronic applications, among which hydrogels based on PEDOT:PSS are particularly promising owing to their favorable electrical, mechanical properties, and biocompatibility. Despite recent developments of various PEDOT:PSS hydrogels, several challenges still remain as unresolved questions in the field. For example, electrical conductivity of poly(2,5-dialkyl)-PPV-based hydrogels are typically low (less than 1 S cm\(^{-1}\)) and their poor adhesion with other engineering solids significantly limits their utility in bioelectronic device applications. Moreover, the limited set of accessible advanced fabrication strategies for PEDOT:PSS hydrogels further restrain their impact in applications. In this talk, we will discuss our series of recent developments on preparation, robust adhesion, and 3D printing of highly conductive PEDOT:PSS hydrogels. We start with a simple yet effective method to prepare highly conductive pure PEDOT:PSS hydrogels. Then, we will discuss a novel strategy to facilitate robust bonding of PEDOT:PSS hydrogel on various commonly used device substrates. Lastly, we will discuss the development of a novel direct ink writing 3D printable PEDOT:PSS ink and the resultant printed structures, uniquely enabled by the unprecedented 3D printing capability.

10:30 AM EP06.07.08
N-Doped Polythiophene Based Polymers for n-OECTs Zivudmorn Khan, Suhao Wang, Mikhail Vagin, Magnus Berggren, Simone Fabiano and Xavier Crispin; Department of Science and Technology (ITS), Linköping University, Norrköping, Sweden.

Organic electrochemical transistors (OECTs) are captivating significant attention owing to their applications in various fields such as molecular sensing, neuromorphic computing, digital logic circuits, cell culture analysis and printed electronics. However, building complementary circuits requires high-performance complementary p-type (hole-transporting) and n-type (electron-transporting) materials. Up to date, most reported OECTs are based on p-type polymers, with n-type lagging far behind mainly due to the lack of efficient and stable n-type conducting polymers. Herein, we report that polythiophene based polymers specifically poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3-alkylthiophene-2,5-diyl) (P3HT) conventionally p-type electrochemically can be doping to be n-type. The electronic conductivity of both PEDOT and P3HT was estimated to be 744 and 640 mS cm\(^{-1}\), respectively. Both, PEDOT and P3HT can work successfully as efficient n-type channel material for OECTs.

10:45 AM EP06.07.09
A Simple Technique to Reduce Contact Resistance in Organic Field-Effect Transistors Zachary Lampert1, Katrin Barath1,2, Hyunsu Lee1, Eliot Gunn1, Sebastian Engmann1, Hu Chen1, Martin Guthold1, Iain McCulloch1,3, John Anthony1,2, Lee Richter1, Dean DeLongchamp3 and Oana Juretescu1; 1Department of Physics and Center for Fundamental Materials, Wake Forest University, Winston Salem, North Carolina, United States; 2Department of Biomedical Engineering, Duke University, Durham, North Carolina, United States; 3Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; KAUST Solar Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 4Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 5Department of Chemistry, University of Kentucky, Lexington, Kentucky, United States.

Contact effects represent a significant hurdle in the pursuit of the promised potential of organic thin-film transistors (OTFTs). For effective use in radio-frequency identification (RFID) and the other myriad technologies commonly ascribed to OTFTs, devices must operate in the high kHz to low MHz range, which requires a combination of high-mobility semiconductor and short channel length. However, transistors with short channel lengths must be accompanied by a drastic reduction in contact resistance. The channel conductance scales with channel length, whereas contact resistance is independent of this reduction in scale and, without a proportional decrease in contact resistance, results in a reduced effective device mobility. For these reasons, the development of functional devices based on organic semiconductors requires significantly diminished contact resistance.

In this work, we focus on a simple, yet effective method to engineer OTFT electrodes with exceptionally low contact resistance and high device performance. We fabricate staggered-structure OFETs in the bottom-contact, top-gate configuration using Ti/Au source and drain contacts treated with pentafluorobenzeneiodithiol (PFBT), and Cytop as the top-gate dielectric, while as semiconductor we tested both small molecules and polymers. We evaluated the performance of OFETs using the same architecture with contact deposition rates varied between 0.5 Å s\(^{-1}\) and 2.5 Å s\(^{-1}\). In 2.8-difluoro-5,11-his-triethyl(ethylenyl) anthradithiophene (dif-TES ADT) devices we found an increase in mobility from \(\mu = 3.7 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}\) obtained at a rate of 2.5 Å s\(^{-1}\) to \(\mu = 19.2 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}\) at 0.5 Å s\(^{-1}\) Similarly, in the copolymer indacenodithiophene-co-benzothiadiazole (C4DT-BT), the mobility increases from \(\mu = 3.3 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}\) at 2.5 Å s\(^{-1}\) to \(\mu = 12.0 \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}\). To determine if these results were due to a difference in semiconductor film microstructure, we performed microbeam grazing incidence wide-angle X-ray scattering (\(\mu\)GIWAXS) and NEXAFS but find no significant differences. We assessed the contact resistance of these devices using the gated transmission line method (gated-TLM) and find that the largely improved mobility at 0.5 Å s\(^{-1}\) coincides with a significant reduction in contact resistance, with the lowest value of 200 Ω cm being obtained in the polymer devices. From scanning Kelvin probe microscopy, we discovered that the origin of the reduced contact resistance is the presence of high work function surface domains resulting from local SAM order, that facilitate injection into the semiconductor. The massively improved performance in both small-molecule and polymer semiconductors indicates that the reduced rate of source and drain contacts is an important parameter to modify in order to reach the low contact resistances necessary for the integration of OFETs into existing technologies.1

Lampert et al., Nature Commun, accepted

11:00 AM EP06.07.10
A New Concept of Electrode for Highly Efficient Ambipolar Carrier Injection in Organic Semiconductors Katsumi Tanigaki1,2, Thangavel Kanagasekaran1,2, Taiki Miura1 and Hidekazu Shimotani1; 1Department of Physics, Graduate School of Science, Tohoku Univ, Sendai, Japan; 2Department of Physics, WPI-AIMR, Sendai, Japan.

Carrier injection from metal electrodes to semiconductors and electrical transport in semiconductor active layers are the most two important key actions in electronic devices. Generally, two types of semiconductors can be considered: One being semiconductor (OSCs) based on carbon based molecules and the other being inorganic semiconductors (ISCs). The former has a clean surface without dangling bonds in π-bonded system, and the latter is in a σ-bonded one and frequently has dangling bonds on its surface and metal-semiconductor interface structure. Such a phenomenon is known as Fermi level pinning leading to a vacuum level shift at the MS interface known as the Bardeen limit. The former has a clean surface without dangling bonds in π-bonded system, and the latter is in a σ-bonded one and frequently has dangling bonds on its surface and metal-semiconductor interface structure. Such a phenomenon is known as Fermi level pinning leading to a vacuum level shift at the MS interface known as the Bardeen limit. Generally, two types of semiconductors can be considered: One being organic semiconductors (OSCs) based on carbon based molecules and the other being inorganic semiconductors (ISCs). The former has a clean surface without dangling bonds in π-bonded system, and the latter is in a σ-bonded one and frequently has dangling bonds on its surface and metal-semiconductor interface structure. Such a phenomenon is known as Fermi level pinning leading to a vacuum level shift at the MS interface known as the Bardeen limit.

1, 2

Carrier injection and transport in semiconductor active layers are the most important key actions in electronic devices. Generally, two types of semiconductors can be considered: One being semiconductor (OSCs) based on carbon based molecules and the other being inorganic semiconductors (ISCs). The former has a clean surface without dangling bonds in π-bonded system, and the latter is in a σ-bonded one and frequently has dangling bonds on its surface and metal-semiconductor interface structure. Such a phenomenon is known as Fermi level pinning leading to a vacuum level shift at the MS interface known as the Bardeen limit. Generally, two types of semiconductors can be considered: One being organic semiconductors (OSCs) based on carbon based molecules and the other being inorganic semiconductors (ISCs). The former has a clean surface without dangling bonds in π-bonded system, and the latter is in a σ-bonded one and frequently has dangling bonds on its surface and metal-semiconductor interface structure. Such a phenomenon is known as Fermi level pinning leading to a vacuum level shift at the MS interface known as the Bardeen limit.
Low-voltage Organic Field-Effect Transistors Printed on Plastic Operating Above 10 MHz

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1Politecnico di Milano, Milano, Italy; 2Istituto Italiano di Tecnologia, Milano, Italy.

Printed polymer field-effect transistors (FETs) have been considered for many novel applications towards large area and flexible electronics, since they can enable pervasive integration of electronic functionalities in all sorts of appliances, their portability and wearability. However, printed polymer FETs fabricated with scalable tools fail to achieve the minimum speed required for example to drive high-resolution displays or to read the signal from a real-time imager, where a transition frequency (fT) i.e. the highest device operating frequency, above 10 MHz is required. Such a goal is even more critical to achieve with low operating voltages and on cheap plastic foils. Here, we demonstrate that high-frequency, low-voltage, polymer field-effect transistors can be fabricated on plastic with the sole use of a combination of scalable printing and digital laser-based techniques. These devices achieve fT in the MHz range already at 2 V, and reaches a record 14 MHz at 7 V. These devices can be successfully integrated into a rectifying circuit on plastic operating at 13.56 MHz, allowing to supply a DC voltage to RF devices and tags fabricated with cost-effective production processes.

Printed Low Voltage Organic Field-Effect Transistors and Circuits on Paper Substrate

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Recently, electrical devices based on paper or paper-like substrates have attracted considerable attention as a possible next-generation technology capable of replacing plastic-based electronics. Indeed, compared with conventional flexible substrates employed in electronic devices, paper features ubiquity, extremely low costs, eco-sustainability, as well as flexibility and bendability. Thank to these merits, in the last years the use of paper or paper-like substrates has been explored in different applications, ranging from basic electronic components to complicated devices and circuits. Basic electronic component are essential in every paper electronics application. In particular, the transistor is the fundamental component in most electronics systems. In order to develop flexible paper electronic devices, inexpensive and highly efficient fabrication methods are necessary. Printing techniques, such as inkjet printing, has gained a growing interest for depositing functional materials. Thank to scalability and manufacture cost, inkjet printing on paper is more competitive than other approaches. However, so far only few works report about thin film transistors (TFTs) printed on paper substrates. In this work, a low voltage organic field effect transistor (OFET) fabricated by inkjet printing on paper is presented. In particular, Bottom Gate- Bottom Contact devices were fabricated. A PEDOT:PSS-based commercial ink was employed for patterning gate, source and drain contacts by means of inkjet printing. A thin film of Parylene C has been deposited as organic insulator by means of chemical Vapour Deposition. Finally, a p-type organic semiconductor, namely PEDT-Pentacene, was inkjet-printed through an homoe-made ink. Alternatively, an n-type organic semiconductor, namely Alq3, was deposited by spin coating. All devices were fabricated on a p-e:smart paper type 2 from Felix Schoeller. This is a 185 ± 10 µm thick flexible paper-based substrate covered with a nonporous surface coating and a hydrophile primer layer. Reproducible electrical performances were obtained on a set of more than 50 devices. In particular, low operating voltages (as high as 5 V), significant charge carrier mobility (in the range 0.4 cm²/Vs for p-type OFETs and 0.01 cm²/Vs for n-type OFETs), and a quasi-zero threshold voltage were recorded. Taking advantage on the fact that both p-type and n-type OFETs have been fabricated, complementary electronic circuits have been successfully fabricated and tested. In particular, complementary inverters with a valuable gain (10 V/V) and noise margins (of about 2 V) were initially fabricated. Starting from such basic building blocks, other logic ports, namely AND, OR, NAND and NOR, were fabricated and tested. These results pave the way for a future development of complex electronic systems that can be fabricated on paper by means of cost-effective techniques and with enhanced properties of portability (enabled by low voltage operation) and functionality (enabled by complementary circuit logic).
Isotropic Self-Assembly Process of a Low Crystalline Interactions

Ray Diffraction (GIXRD) analysis revealed that the orientation of the oCVD PEDOT film is dependent on the deposition temperature and (P/P0) orientation of oCVD PEDOT changed from predominantly edge-on orientation (h00) to predominantly face-on orientation (0K0) with an increase in deposition temperatures and a decrease in P/P0 of the oxidant vapor. The optical properties of oCVD PEDOT are of essential importance for application as transparent conductors while there is a trade-off between transparency and sheet resistivity. It was found that the figure of merit (FOM) which is defined as the ratio of direct current conductivity (σdc) to optical conductivity (σop) increases by a decrease in P/P0 of the oxidant vapor.

Meniscus-Guided Large-Area Thin-Film Formation of Organic Semiconductors with Crystallization Control

The electronic properties of solution-processable small molecule organic semiconductors have rapidly improved in recent years, rendering them highly promising for various low-cost large-area flexible electronic applications. Here we present solution shearing as a promising technique to increase the electron mobility (μe) of a low crystalline polymer. We demonstrate this approach using NDI-based copolymers (PNDI-FTVT), with dithienylethene having the 3-position instead of hydrogen. The two fluorene substituents on the FTVT unit impart a dipole moment in the polymer backbone, leading to a fast and robust aggregation process (mainly a kinetic process), which suppresses NDI-driven self-assembly process (a thermodynamic process). This kinetic process limits the growing crystals; thus, the resulting smaller crystals improve electrical connection between crystal domains. In addition, robust aggregates driven by FTVT units in amorphous domains afforded a thermally stable morphology in the solid state. This microstructure resulted in improved μe of transistor devices by lowering energetic disorder as well as the reinforced film morphology at elevated temperature.

Scalable Fabrication of Highly Crystalline Organic Semiconductor Thin-Film Array by Screen Printing

Screen printing has been widely applied in electronic industry, since it has several distinct advantages such as large scale, low temperature processability, low cost and efficient productivity. However, due to the requirement of high viscosity of ink, and the relatively large printed film thickness, screen printing is usually used to fabricate metal electrode, while it remains a significant challenge to fabricate high quality organic small molecule semiconductors (OSCs) crystalline film. Herein, a simple method for the fabrication of organic semiconductors, in which the high throughput and target productivities are essential, is presented, which employs solution shearing technique to generate high quality organic thin-films for organic transistors. In this presentation, an example of an additive manufacturing approach for electronics that integrates processes such as fused-deposition modelling, paste extrusion, ink-jet printing, and pick-and-place, as well as in-line metrology methods will be described. Using these tools and techniques a number of printed and hybrid devices have been made including: 1) simple organic-based logic circuits were demonstrated using our technique.

Achieving Outstanding Thin-Film Deformability of Semiconducting Polymers Through Modulating Molecular Packing in Nanoscale

Polymer semiconductors nowadays have been investigated for use in future electronics that have good electrical performance, mechanical compliance and large scale processability. The performance of polymers has been enhanced by designing molecules with improved electronic and mechanical properties. Although comparable electrical performance to traditional inorganic semiconductors can be achieved by polymeric semiconductors, it is still challenge to simultaneously introduce stretchability at the molecular level, in order to create mechanically robust semiconducting polymers. Typically, mechanical resilience and ductility of polymer active thin layer can be tailored through chemical design, such as inserting functional units in polymer backbone or manipulating alkyl side chains. However, such methodologies involve complicated chemistry process, and triggered batch-to-batch variations. We therefore develop a new approach by physically adding organic small molecules, which possess high boiling point and low vapor pressure, into semiconducting polymers. By delivering such small molecules between polymer chains, the lamellar packing distance of semiconducting polymer can be modulated from 24.6 Å to 27.9 Å. This 3 Å volume opening using our method indeed greatly improve the thin film deformability due to the enhanced polymer chain dynamics in nanoscale. The semiconducting film can be stretched up to 300% without cracks. Finally, a charge carrier mobility of 1.8 cm2/V·s is achieved as the active layer stretched under 100%, which is one of the best performance among stretchable polymer semiconductors in the research community.

Scalable Fabrication of Highly Crystalline Organic Semiconductor Thin-Film Array by Screen Printing

Screen printing has been widely applied in electronic industry, since it has several distinct advantages such as large scale, low temperature processability, low cost and efficient productivity. However, due to the requirement of high viscosity of ink, and the relatively large printed film thickness, screen printing is usually used to fabricate metal electrode, while it remains a significant challenge to fabricate high quality organic small molecule semiconductors (OSCs) crystalline film. Herein, a simple method for the fabrication of
various small-molecular OSCs crystalline film using ultra-low viscosity OSCs/insulating polymer blends by screen printing is reported. The film thickness is reduced to tens of nanometers by tuning the squeezing velocity and concentration of ink. Meanwhile, the quality and crystal domain size is largely improved by using screen printed banks prior to printing to confine OSCs crystallization and minimize nucleation sites, resulting in higher devices performance. As a result, the as-prepared C71-BTBT organic field-effect transistors (OFETs) and device array achieved an excellent performance with the highest hole mobility up to 12.10 cm² V⁻¹s⁻¹, and the on/off ratio is up to 8×10⁶, which is on par with its single crystal counterparts. In addition, the uniform distribution of mobility in 8×8 array indicated the scalability of this method. Meanwhile, this method can also be applied for other OSC materials such as C71-DPA. The high-performance OFET device demonstrated that screen printing is suitable for the scalable manufacture of organic electronic circuit. The successful fabrication of organic semiconductor layer by printing method is the key step toward full printed flexible electronics.

### Structure Formation in High Performing Organic Transistors

**Lee Richter**, Dawei Wu, Maria Kaplan, Hyun Wook Ro, Sebastian Engmann, R. J. Kline, Daniel Fischer, Dean DeLongchamp, Eliot Gann, Lars Thorsen, Christopher McNeill, Juliaanna Pance, and Thomas D. Anthopoulos; National Institute of Standards and Technology, Gaithersburg, Maryland, United States; Theis Research, La Jolla, California, United States; Australian Synchrotron, Clayton, Victoria, Australia; Monash University, Clayton, Victoria, Australia; Imperial College London, London, United Kingdom; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

As the demand for high performance displays increases, the required performance for solution processed transistors for backplanes has increased. Target mobilities to drive AMOLED displays are now in the 10 cm² V⁻¹ s⁻¹ range, competitive with amorphous oxides. While advances in materials continue, over-all ink design and film processing present additional opportunities for device improvement. Two general approaches to improved devices have emerged: production of aligned channels via directional coating and production of vertically structured channels from blend-based inks. Using insitu X-ray and optical probes, we will explore the development of structure in these platforms. Due to the pi-stacking motif of most semiconducting polymers, the local mobility is intrinsically anisotropic. Therefore fabrication of aligned films enables further optimization of device performance. Blade coating is an excellent prototyping tool for production deposition techniques such as slot die coating and, due to its direction character, can result in aligned films. We report results from blade coating a number of high performing polymer materials. Depending on polymer and deposition regime, highly aligned films can be produced. The aligned films typically exhibit significant (c.a. 5 times) greater mobility than isotropic films. Detailed morphological studies suggest that the improvement in transport is related to alignment of the inter-crystallite regions (tie-chains). In-situ studies indicate that the coating induced alignment nucleates near the air interface and is facilitated by the presence of a lyotropic liquid crystal phase. In blend-based inks, vertical segregation between the active material and the matrix can result in advantageous ordering at either the buried or air interface. This can lead to improved device performance in either bottom or top gate architectures. In-situ probes again provide detailed insights into the development of vertical stratification and active layer crystallization.

**SYMPOSIUM EP07**

Next-Generation Interconnects—Materials, Processes and Integration  
April 23 - April 25, 2019

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**SESSION EP07.01: Dielectrics—New Insights I**

**Session Chairs:** Silvia Armini and Vincent Jousseaume  
Tuesday Morning, April 23, 2019  
PCC North, 200 Level, Room 221 B

**10:30 AM *EP07.01.01***

5nm and Beyond BEOL (Back End of the Line) Interconnect and Heterogeneous Integration Strategies to Continue Moore’s Law Scaling  
Lawrence Clevenger; IBM T.J. Watson Research Ctr, Albany, New York, United States.

As semiconductor technology nodes scale towards 3 nm, there are acute difficulties in achieving interconnect scaling due to novel device architectures and dimensionality, design, performance and reliability issues. There are key interconnect scaling and packaging heterogeneous integration strategies for future technology nodes. Co-optimizing these strategies determines the overall best definition to enable continued Moore’s law scaling.

For future semiconductor nodes, the ability of optical patterning to support the required interconnect pitches is in doubt. This is the driving factor for the introduction of EUV lithography to continue dimensional scaling. Even with EUV patterning, there are additional design methodology challenges such as the lack of wiring track level reduction due to process related block level scaling issues. From a traditional materials science perspective, BEOL resistance and capacitance is a significant portion of the parasitic degradation of overall technology performance. As physical wire and via sizes decrease, BEOL resistance increases exponentially with decreasing area due to surface and grain boundary scattering and a lack of scaling for Cu diffusion barriers such as TaN. Challenges for BEOL capacitance include integration issues which drive the effective dielectric constant higher than the modeled values. BEOL reliability is challenged by operation voltage requirements and by novel device architectures which strain electromigration and dielectric breakdown performance.

To mitigate these challenges and continue Moore’s law scaling, novel design methodologies decrease the number of wiring tracks in standard cell libraries and increase the wiring levels to improve both performance and density. EUV lithography is replacing optical lithography to enhance design and performance, requiring fewer design rule restrictions, improving patterning tolerances, and enabling bi-directional metal and process simplification. Hardware teams will implement novel processes to enable recovery of resistance and capacitance scaling and to support electromigration and time dependent dielectric breakdown reliability. These patterning and process improvements are needed to support novel device architectures in technologies such as scaled FinFET and Stacked-Si-Nanosheets.

To further mitigate challenges in interconnect scaling, heterogeneous integration of IP has been migrating from SoC (System on a Chip) to SIP (System in Package). This introduces the challenge to use novel packaging techniques with high density interconnects to achieve enhanced functionality and improve bandwidth and latency. There are novel architectural, integration and material related innovations that address the challenges for the continuing enablement of Moore’s law scaling.

**11:00 AM *EP07.01.02***
Amorphous low-dielectric constant (low-$k$) and high-dielectric constant (high-$k$) materials have dominated the nanoelectronic materials research scene over the past decade, but have recently reached a state of maturity and perhaps their scaling limits. Based on this, one may ponder the direction of nanoelectronic dielectric materials research and the future of the field. However, as we will clarify, there is still plenty of room to grow!

In this address, we seek to illustrate that high-$k$ and low-$k$ dielectrics represent just a tiny fraction of the numerous dielectric materials utilized in nanoelectronic products and that numerous new applications for dielectric materials are emerging as the industry transitions to novel patterning schemes and prepares for life post CMOS scaling. We will begin by briefly exploring the entirety of dielectric materials utilized in advanced nanoelectronic products with a particular focus on often ignored etch stopping, diffusion barrier, and passivation dielectrics and their more specialized requirements. We will then transition to examining the various novel pitch division schemes being developed to cope with the delay of EUV lithography and the abundant new dielectric material applications these schemes create. We will specifically focus on the various new spacer and hard mask dielectrics that pitch division requires, their colorful etch selectivity requirements, and suggest future research needed to enable even more exotic patterning schemes. We will further examine how what was once old can become new again and specifically explore how both high-$k$ and low-$k$ dielectrics are being utilized to fill the needs of future beyond CMOS devices. In particular, the application of high-$k$ and low-$k$ dielectrics in novel resistive switching device applications will be examined. We will conclude by reviewing the unique obstacles that dielectric materials present for the realization of advanced cryogenic quantum computing architectures and the necessary associated research vectors to prevent dielectrics from becoming quantum computing’s Achilles heel.

11:30 AM EP07.01.03  
Molecular Design of Ultrastiff ULK Dielectric Hybrid Films—Implications of Network Connectivity and Precursor Geometry  
Karsu I. Kliche and Reinhold Daußard; Stanford University, Stanford, California, United States.

The successful integration of ULK dielectric films into microelectronic device interconnects has been challenging due to their poor thermal and mechanical properties. We have developed computational tools to investigate the fundamental molecular level parameters controlling the properties of these materials, and also have shown that they exhibit very surprising phenomena ranging from asymmetric elastic behavior to non-affine deformations, and can be engineered to exhibit time dependent inelastic deformation characteristics. In this work, through molecular dynamics simulations we present new design strategies at the molecular level focusing on two unique ways to effectively enhance the mechanical properties: Firstly, we demonstrate how hyperconnected networks with a connectivity exceeding the chemical coordination number of silicon increase elastic modulus. Secondly, we show how hyperstiff precursor molecules themselves with specific geometrical features, which have not been previously considered, can be exploited to further reinforce the rigidity of hyperconnected films. We define a hyperstiff precursor as one with a cyclic planar organic group, an example of which is triethoxysilyl benzenne (1,3,5-benzene).

The impact of utilizing these two main parameters is such that we are able to design ultrastiff hybrid films with a modulus that goes beyond that of fully dense silica, while still maintaining an ultra low density and dielectric coefficient. One immediate implication of the design of these ultrastiff hybrid networks manifests itself as a new and highly effective method to improve the mechanical robustness of nanoporous hybrid films. Our results show that the nanoporous films designed with an ultrastiff hybrid matrix lead to three to four times increase in the elastic modulus compared to porous films with traditionally bridged network containing less stiff organic chains, such as ethane-bridged oxycarbosilane (Et-OCS). This substantial increase in the stiffness of nanoporous hybrid films is a crucial step taken to minimize the limitations due to poor mechanical properties, thereby allowing for new opportunities to fully benefit from the ultra low dielectric constant of porous thin films.

11:45 AM EP07.01.04  
Polysiloxane Thin Films Deposited by iCVD—Application to Through-Silicon via Insulation  
Vincent Jousseaud, Celine Ribiere, Gilles Romero, Pierre-Emile Philip, Daniel Scvelo, Yorrick Exbrayat, Antonio Roman, Christophe Lieitra, Stephane Minoret, Sophie Verrun, Bruce Altenmus, Thierry Mourier, Jacques Faguel, Université Grenoble Alpes, Grenoble, France; CEA, LETI, Grenoble, France; Tokyo Electron Europe Limited, Meylan, France; Tokyo Electron US Holdings, Albany, New York, United States; Tokyo Electron US Holdings, Austin, Texas, United States.

Three-dimensional integrated circuit (3 IC) integration attracts much attention because it has the potential to enhance IC performance and allows the integration of heterogeneous devices [1]. One approach consists in stacking vertically several chips which are electrically connected with through-Si vias (TSVs). Among the different ways to create TSVs, via-middle integration allows the TSV realization between the front end of line and the back end of line (BEOL) while TSVs are built after the BEOL in via-last integration. One of the key steps in the TSV fabrication is their electrical insulation from the silicon substrate. Usually, SiO$_2$ deposited by Plasma-Enhanced CVD or by Sub-Atmospheric CVD depending on the integration scheme, is used as the TSV-liner material. However, the use of SiO$_2$ presents some limitations in order to realize advanced 3 IC, such as a poor step coverage (using PECVD) and higher dielectric constant compared to the low-$k$ interlayer dielectric material of BEOL. Through-silicon via with polymer liners has attracted attention because these polymers have a low dielectric constant and their expected mechanical compliance can enable higher TSV integration by suppressing the TSV-induced stress [2]. However, even though several demonstrations were published in the literature, the TSV insulation using organic polymers is not yet adopted in this work, organosiloxane thin films were deposited by initiated Chemical Vapor Deposition (iCVD). This deposition technique, which is a low-energy (no plasma) and solvent-free method, allows to deposit organic or hybrid polymers at low substrate temperature, thus compatible with the TSV-last thermal budget requirements. Poly(V3D3) thin films were deposited from trivinyl-trimethyl-cyclo-trisiloxane as the monomer and tert-butyl-oxide as the initiator. First, the impact of process conditions on the deposition rate, chemical composition and step coverage was investigated. A combination of FTIR, ellipsometry, ellipsometric porosimetry, ToF-SIMS analysis, SEM and electrical characterizations was used to characterize the structure and the properties of the films. It is shown that poly(V3D3) thin films deposited at low temperature (typically lower than 100°C) can present low dielectric constant (down to 2.7) with conformality close to 50% in 10*100 μm TSVs. Moreover, the impact of annealing on the thermal stability of the films was studied. After appropriate curing (thermal-only or UV-assisted), the dielectric film is stable up to 400°C. Finally, a full TSV integration was completed (via-middle 100°C) can present low dielectric constant (down to 2.7) with conformality close to 50% in 10*100 μm TSVs. Moreover, the impact of annealing on the thermal stability of the films was studied. After appropriate curing (thermal-only or UV-assisted), the dielectric film is stable up to 400°C. Finally, a full TSV integration was completed (via-middle 100°C).

material candidates and integration schemes.

2:00 PM EP07.02.02
**Intermetallic Compounds as Possible Cu Alternatives**

Junichi Koke, Linghan Chen, Daisuke Ando and Yuji Sutou; Department of Materials Science, Tohoku University, Sendai, Japan.

In local interconnection of advanced LSI, copper alternative materials have been sought to mitigate the increase of Cu line resistivity with decreasing line width. The required properties for the alternatives are small value of $\tau_{0}$, i.e. low resistivity in narrow lines, low diffusivity for good electro-migration resistance under high current density, low melting temperature for easy grain growth at low process temperature, small Young’s modulus for easy CMP. Proposed materials to date include pure metals, alloys, carbides, nitrides, and silicides. In addition, low and stable material cost is an important factor to be considered. To provide feasible alternatives which satisfy these properties, we focus intermetallic compounds. For example, NiAl is an ordered bcc compound having a bulk resistivity of 9 mW-cm. It is a well-known heat resistant material having a high melting point of 1638 °C, thus a good electromigration reliability may be expected. Furthermore, NiAl has a large cohesion energy of ≈568 kJ/mol, hence the interdiffusion and detrimental reaction of individual Ni or Al ions with Si and SiO <sub>2</sub> may be suppressed. In addition, Al oxide has heat of formation of ≈1678 kJ/mol, much higher than ≈911 kJ/mol of SiO<sub>2</sub>, so there is a tendency for Al atoms to bond with O atoms at the NiAl/SiO<sub>2</sub> interface, possibly leading to good adhesion. Experimental results showed good adhesion and no interdiffusion between NiAl film and SiO<sub>2</sub>/Si substrate. Similar results were obtained in other selected intermetallic compounds. The possibility of intermetallic compounds will be discussed in detail as the Cu alternative.

2:30 PM EP07.02.03
**The Effects of Dioxide Molecules on the Electrodeposition of Cobalt**

Qiang Huang, Yang Hu, Tyler Lyons and William Sides; University of Alabama, Tuscaloosa, Alabama, United States.

Electroplated damascene copper has been used for more than 20 years for interconnects in semiconductor and microelectronic industry[1]. As the structures continue to scale, the coarse grains formed during annealing become increasingly difficult to fit into the fine structures, resulting in higher resistance and poorer electro-migration[2]. In addition, as the dimension of structure approaches or falls below the electron mean free path of copper, the resistivity exponentially increases[3], demanding a material change for future technologies. This talk presents fundamental studies on the electrodeposition of cobalt in presence of a class of organic additives, dioxime, to modulate the deposition rate and impurities in cobalt. Suppression of cobalt deposition was observed upon the addition of dioxime molecules and such suppression effect was found to result from an adsorbed Co-oxime complex structures, which breaks down upon the application of more negative bias. Such break down not only kicks off the deposition of cobalt but also results in the incorporation of impurity elements, such as Carbon, Hydrogen and Oxygen. The nucleation and growth at the beginning of deposition was studied, aiming to understand the limitation on the formation of continuous cobalt films. A two-step nucleation phenomenon was observed for the first time due to the reduction reactions from the chelates and free cobalt ions. A second chemical species was used to purposely introduce different impurity elements into the deposited Co films, aiming to understand the effects of different impurities on the grain structure of cobalt.

REFERENCES


2:45 PM EP07.02.04
**The Formation of Nano-Voids in Electroless Cu Layers**

Tobias Bernhard; Electronics PTH, Atotech Deutschland GmbH, Berlin, Germany.

The electrical reliability of multilayer HDI/BGA-PCBs<sup>1</sup> is mainly affected by the thermo-mechanical stability of stacked micro via interconnections. Here, a critical failure mode is the stress related crack between the electrolytically filled via and the target pad, commonly known as target pad separation. The junction includes two Cu-Cu-interfaces, one between the target Cu pad and the thin electroless Cu layer and the second between electroless Cu and electrolytic Cu.

Large nano-voids (with dimensions of several ten to several hundred nm) and inhibited Cu recrystallization across the interfaces are the two main indications of a weak link to the target pad. These failures are mostly related to insufficient etching and cleaning of the target pad or persistently adsorbed organic residues at the sputtered Cu-surfaces and are well observable via standard inspection tools such as cross-sectioning and electro or ion-polishing in combination with SEM<sup>2</sup>. Recently, closer inspections of such junctions were performed via Transmission Electron Microscopy on thinned lamellas down to 50-60 nm. In a transmission mode of TEM (HAADF<sup>3</sup>-mode) a substantial density (up to 30000 µm<sup>-2</sup>) of circular shaped “black spots” were found with diameters of lower than 10 nm, i.e. below the spatial resolution of commercial FIB/SEM<sup>4</sup>-tools. These “black spots” are localized within or closed to the electroless Cu-layer.

In the first part of the paper we will present HR-STEM, XEDS<sup>5</sup> and EF-TEM<sup>6</sup> measurements, in order to identify the origin of the “black spots” in the TEM-images. Here STEM/HAADF and Bright-Field TEM point to less material inside of these “black spots”, whereas energy filtering TEM indicates less average lamella thickness within the features. In combination with XEDS-mapping, where no chemical composition difference between the spot region and the Cu-bulk region was found, we conclude that the observed black spots are most likely voids. To evaluate the impact on the junction reliability and to find probable root causes of this newly discovered void-phenomenon, an extensive field study of more than 400 TEM investigations was performed. TEM in combination with XEDS enables the localization of the electroless Cu layer in the junction by detecting the codeposited Ni (typ.: 0.2-1.5 at%<sup>5</sup>) and a precise assignment of the nano-void affected interfaces or layers.

This nano-void field study comprised the investigation of HDI and BGA-multilayer PCBs with stacked vias produced by several industry partners and single layer reliability test boards produced in industry like on-site facilities (Atotech Techcenters), accompanied by some laboratory plating tests. Different types of industrially relevant electroless Cu pretreatments, Pd-activator systems, electroless Cu baths and filling Cu-electrolytes were included in the test matrix, as well as the impact of subsequent thermal treatments (one to ten IR-reflow<sup>7</sup> cycles).

Based on this field study, we will present in the second part of the paper a classification of the most relevant nano-void phenomena, determined by the affected interfaces/layers and their appearance after plating or subsequent thermal treatments (IR-reflow). Formation mechanisms and root causes will be discussed as well.

<sup>1</sup>HDIB-High Density Interconnections, BGA-Ball Grid Array, PCB-Printed Circuit Board, IR-Infra Red

3:00 PM BREAK

3:30 PM EP07.02.05
**Reliability Statistics for Next-Generation Interconnects—The Combination of Physical Modeling and Statistical Techniques**

Shinji Yokogawa; The University of Electro-Communications, Chofu, Japan.

The accurate reliability prediction in the development phase is one of the big challenges to achieve the next generation of interconnects. Moreover, for the early adoption of the technologies, the early failure due to process variability defects and a late failure determined by the intrinsic characteristics of materials should be evaluated and improved simultaneously. However, it is difficult to evaluate them accurately for the less-mature technology because of production performance variabilities and small size experiments. The combining of physical modeling and statistical techniques is one of the approaches to solve the lack of stabilities. Conventional statistical methods to estimate chip-level reliability are described with a competing policy, as the weakest link. Underlying features of the lifetime characteristics are explained by the distribution functions that have
definite shape and scale parameters like Weibull and Lognormal distributions. These functions well describe the intrinsic lifetime characteristics but do not express the impacts of the degree of completion. Recently, the distribution families that have two shape parameters is applied to understand and explain the variability impacts. To utilize them effectively, the correlation between the physical mechanism of failure and the shape of distribution must be considered theoretical and experimental.

In this talk, two applications of the statistical distribution are introduced about the lifetime of back-end reliability. The first application is a time-dependent dielectric breakdown (TDDB) under defect clustering condition in back-end-of-line (BEOL) and middle-of-line (MOL) explained by the generalized Burr type XII distribution (GBXII). Because the decrease in spacing has become too excessive, impacts of process variations on product yield and reliability have also become much pronounced. The spacing variation represents the variation of reliability stress and accelerates the breakdown phenomenon around a small space called the "clustering defect." Therefore, understanding the defect impacts on lifetime distribution provides information on not only reliability estimation but also the process variability and TDDB in BEOL and MOL. The GBXII has two shape parameters and, one of them is the clustering parameter that indicates the degree of the defect clustering. A statistical method for the GBXII analysis on TDDB will be introduced.

The second application is a simple prediction method for chip-level electromigration based on segment lifetime. From the distribution of segment lifetime and current density, the chip-level lifetime distribution is approximated by the generalized gamma distribution (GGD). The second shape parameter of the GGD can indicate whether the chip-level distribution is close to the lognormal or Weibull distribution in conjunction with lifetime variation due to process fluctuation and circuit size. Proposed method using GGD can provide the prediction of the chip-level electromigration lifetime for a novel technology without a real circuit design. These approaches enable to understand impacts of the process variation and the circuit size. It will provide the necessary information for the early adoption of the novel technology to use.

EP07.02.06 The Effect of Electrical Current Stressing on Microstructure and Properties of Sn You-Chi Meng, Chien-Lung Liang and Kwang-Lung Lin; Material Science and Engineering, National Cheng Kung University, Tainan, Taiwan.

Electric current stressing has been reported to affect the microstructure of metallic materials along with the variations in mechanical properties and other material performance. The electric current stressing can facilitate recrystallization behavior and thus lower the recrystallization temperature of metals. In the present study, the microstructure-properties correlation of pure Sn metals induced by electric current stressing was investigated. The pure Sn strip was quenched in liquid nitrogen after designed periods and cycles of electric current stressing. The mechanical and electrical properties of the pure Sn strips were investigated using Vickers micro-hardness tester and 4-point probe, respectively. The micro-hardness increases with respect to the current density ranging from 5000 to 6500 A/cm² and reaches a maximum value at 6500 A/cm². The maximum enhancement in micro-hardness shows a 5% increment compared with the value of the as-annealed specimen. However, the electric current stressing at higher current densities (7000 and 7500 A/cm²) lowers the micro-hardness, showing a two-stage mechanical property variation between relatively low current density one (5000-6500 A/cm²) and relatively high current density one (7000-7500 A/cm²). In general, all the electric current stressing conditions investigated were found to enhance the micro-hardness of the Sn strips. Dissimilar to the trend of micro-hardness, the sheet resistance of the pure Sn strip slightly decreases after cycles of direct current stressing. The average grain size and grain orientation of Sn metals were investigated using electron back scattered diffraction analysis. The results show that an increasing number fraction of fine grains, corresponding to a general lowering in grain dimension, with the increasing electric current density at the first stage of relatively low ones (5000-6500 A/cm²). However, grain coarsening was observed at relatively high current densities (7000-7500 A/cm²) due to the Joule heating effect. The activation energy for the two-stage micro-hardness variations induced by electric current stressing was estimated, and the mechanisms behind were further disclosed in this research.
EP07.03.03
Optimizing Growth of TaSe₃ Nanowires via Chemical Vapor Deposition
Aimee Martinez, Thomas Empante, Michelle Wurch and Ludwig Bartels; University of California, Riverside, Riverside, California, United States.

Tantalum triselenide (TaSe₃) is part of the transition metal trichalcogenides (TMTs) family and are of interest due to their high conductivity and low dimensionality. These quasi 1D nanorod structures show promise for future applications as replacement interconnect materials as copper reaches its limits due to surface and grain boundary scattering effects. The main goal of this work is to develop a facile synthesis method and study the properties of these nanorod materials as the cross sections is thinned to the nanometer scale. Here we present a novel chemical vapor deposition (CVD) method which produces TaSe₃ nanorods directly on an SiO₂/Si substrate in under an hour. There nanorods are characterized using Raman spectroscopy and electronic transport measurements revealing their behavior when scaled down to the nanometer scale.

EP07.03.04
Study of the Structure, Electrical Conductivity of Cr-Cu Thin-Film Composition on a Glass Substrate
Sergey M. Karabanov; Ryazan State Radio Engineering University, Ryazan, Russian Federation.

Cu films are widely used for interconnections in microelectronics. In some applications, reliable thin-film connecting elements having high electrical conductivity, mechanical stability and adhesion to the glass substrate are required. In this case the length of the elements amounts to tens of centimeters. In this paper, Cu was used as the basis for the connecting elements. To ensure high adhesion Cr was used as an underlayer. The substrate material was glass made of SiO₂ (73%), Na₂O (13%), CaO (8.5%) and other oxides. Cu and Cr films were applied by thermo-vacuum evaporation at residual pressure in the chamber of 10⁻⁶ – 5×10⁻⁷ mmHg. The structure of the films was analyzed on a JEOL-50A scanning microscope. For the study of defect formation, electron and light microscopes were used.

The paper investigates the structure, electrical conductivity, adhesion, defect formation of Cu, Cu-Cr, Cr-Cu-Cr thin-film conductors. As a result of the conducted research, the regularities of changes of the film structure, electrical conductivity, adhesion, defect formation depending on the technological process parameters were established. Physical and technological mechanisms determining the observed patterns are considered. The research results are used in the technological regulations for the devices production.

EP07.03.06
Effects of Dielectric Curing and Plasma Treatment Conditions on the Interfacial Reliability of RDL for Fan-Out Wafer Level Packaging
Young-Bae Park¹, Gahui Kim¹, Kirak Son¹ and Dogeun Kim²; ¹Andong National University, Andong-si, Korea (the Republic of); ²Korea Institute of Materials Science, Changwon, Korea (the Republic of).

As personal mobile and IoT products are more and more popular, and IC technology is more and more advanced, fan-out wafer level packaging (FOWLP) technology is therefore valued and developed highly. FOWLP is one of the latest trends in microelectronics packaging. FOWLP is a novel concept intended to increase the number of external I/O connections and achieve greater integration within small form factor systems. FOWLP has a high potential in significant package miniaturization concerning package volume but also in thickness. A key ingredient enabling the FOWLP is the redistribution layer (RDL), which rearranges I/O locations. The redistribution layer is a stacked copper-dielectric structure. In fan-out packages, Si chips are directly attached to the RDL, and the molding compound provides the necessary mechanical support. To manufacture these packages, there are several challenging requirements for dielectric materials to be cured at low temperature of (~<250 °C). Low temperature curing requirements for dielectric materials exist since devices embedded with memory chips by the molded compound show low heat resistance, strong adhesion to the copper RDL, stability and adhesion to the glass substrate are required. In this case the length of the elements amounts to tens of centimeters. As a result of the conducted research, the regularities of changes of the film structure, electrical conductivity, adhesion, defect formation depending on the technological process parameters were established. Physical and technological mechanisms determining the observed patterns are considered. The research results are used in the technological regulations for the devices production.

Acknowledgment: This research was supported by MOTIE(Ministry of Trade, Industry & Energy (10067804) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

EP07.03.07
Etch Characteristics of Copper Thin Film Using Continuous-Wave and Pulse-Modulated Plasmas of CH₂COOH/Ar
Chee Won Chung, Jin Su Ryu, Jae Sang Choi, Eun Taek Lim and Moon Hwan Cha; Inha University, Incheon, Korea (the Republic of).

Copper has low leakage and low power consumption due to its lower resistance and faster signal transmission than aluminum. Copper has a high electron migration resistance and is a stable interconnect material. When copper is used as an interconnect, it is prepared by damascene process which includes electroplating and chemical mechanical polishing. Since copper has very low reactivity and copper compounds often have high vapor pressure, it is known to be very hard material to etch using a conventional dry etching. As the critical dimension of the devices is diminished under tens of nanometer, the fatal disadvantages of the damascene process are revealed, which demands the development of novel dry etching technique of copper thin films.

In this study, the etch characteristics of copper thin films masked with SiO₂ films were examined under CH₂COOH/Ar gas using inductively coupled plasma reactive ion etching. The etch rate of copper films and SiO₂ hard mask, and the etch selectivity of copper films to SiO₂ mask, and the etch profile were investigated as a function of CH₂COOH in CH₂COOH/Ar gas. Major etch variables including coil rf power, bias voltages, and the process pressure were applied to evaluate the etch rate, etch selectivity and etch profile.

The evolution of etch profile of copper films in CH₂COOH/Ar was observed to understand the etch process. The optical emission spectroscopy of the plasmas produced from various CH₂COOH concentration in CH₂COOH/Ar was measured to determine the active species in the plasmas. In addition, the energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy for the etched copper surfaces were performed to elucidate the etch mechanism by identifying the copper compounds, if any.

Besides, pulse-modulated plasma has been applied to etch copper films, which has the variables such as the on-off duty ratio and the frequency of the plasma. The effects of pulse-modulated plasma on the etch characteristics of copper were examined. The etching by pulse-modulated plasma is expected to reduce redeposition and etching by-products compared to that by continuous wave plasma.

Acknowledgments This research was supported by the MOTIE(Ministry of Trade, Industry & Energy (10080450) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.
Advanced packaging solutions, particularly 3D integration technologies, are additional boosters for performance and functionality of microelectronic products. However, at the same time, 3D heterogeneous system integration becomes increasingly challenging for product reliability. This talk will address the nondestructive localization and characterization of defects in interconnects to mitigate reliability-limiting effects in 3D IC stacks. Particularly, the geometry of 3D Through-Silicon-Via (TSV)/micro-bump stacks and defects (voids and micro-cracks) in these metallic structures as well as micro-cracks in Cu/low-k Back-End-of-Line (BEOL) stacks caused by thermomechanical stress (Chip-Package Interaction, CPI) will be discussed. We will demonstrate the applicability of sub-micron and nano X-ray computed tomography (XCT) for nondestructive 3D imaging of advanced packaging and BEOL interconnect structures. The shape of solder interconnects and TSV etch profiles are imaged as well. Defects like filling voids in Cu TSVs and micro-cracks in AgSn solder micro-bumps are clearly visualized too using full-chip region-of-interest tomography [1].

Package-induced thermomechanical stress increases the risk of failure caused by delamination along metal/dielectric interfaces or fracture in dielectrics with low fracture toughness in BEOL stacks. The 3D visualization of crack evolution in Cu/low-k interconnect stacks is demonstrated using an experimental setup which combines X-ray microscopy with in-situ mechanical loading. High-resolution 3D image sequences based on nano XCT are acquired during mechanical loading within the X-ray microscope to visualize crack opening and propagation in fully integrated BEOL structures with about 100 nm resolution [2]. As a result, the weakest layers and interfaces are identified, and the robustness of the BEOL stack against chip-package interaction is evaluated. The obtained results provide valuable information for reliability engineering and design-for-reliability (DFR) in semiconductor industry.

Laboratory micro and nano XCT offer intrinsic advantages in the fields of 3D imaging, physical failure analysis, and metrology of electrical interconnects in semiconductor products for both advanced packaging and on-chip interconnect structures by employing a multi-scale approach. Perspectives to overcome two major limitations of state-of-the-art nano XCT tools, i.e. the necessity of sample preparation (typically less than 50 mm thickness, depending on the material composition, if 8 keV photons are used) and low imaging throughput, are discussed. A novel tool concept for X-ray microscopy at high photon energies, using advanced X-ray sources with high flux and the option of multi-energy photons [3], and of advanced X-ray optics with high efficiency at photon energies > 10 keV [4], will be presented.


9:45 AM BREAK

SESSION EP07.04.02
Integration for Superconducting Qubits

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Superconducting qubits are a prime candidate for constructing a large-scale quantum processor due to their lithographic scalability, speed, and relatively long coherence times. As superconducting quantum processors move beyond the few-qubit scale, it will become increasingly important to develop techniques for addressing large numbers of qubits without degrading their performance. 3D integration can alleviate interconnect crowding and enable the construction of large-scale arrays of coherent superconducting qubits. At Lincoln Laboratory, we are pursuing an approach where high-coherence qubits are isolated from a potentially lossy readout and interconnect chip by an intermediate chip with superconducting through-silicon vias. The three-tier stack is bonded using indium bump bonds, which provide structural support and can be used to galvanically connect metal on different chips. We will present our recent work on developing and characterizing critical components for 3D integration, including indium bumps and superconducting through-silicon vias, and discuss progress towards building 3D integrated coupled qubits.

This research was funded by the Office of the Director of National Intelligence (ODNI), Intelligence Advanced Research Projects Activity (IARPA) and by the Assistant Secretary of Defense for Research & Engineering under Air Force Contract No. FA8721-05-C-0002. The views and conclusions contained herein are those of the authors and should not be attributed to the U. S. Government.

9:30 AM EP07.04.03
3D Sequential Technology—Reliability of Cu/low-k Interconnects at High Temperature

Sylvain Beaurepaire1,2, Chloe Guerin1,2, Vincent Jousseaume1,2, Patrice Gomon1,2, Ahmad Bsiemy1,2, Vincent Maurel1,2, Xavier Federspiel1,2, David Ney1 and Claire Fenouillet-Beranger1,2; Université Grenoble Alpes, Grenoble, France; CEA-Leti, MINATEC Campus, Grenoble, France; LTM, UGA/CNRS/CEA, Grenoble, France; CEA-LETI, MINATEC Campus, Grenoble, France; STMicroelectronics, Crolles, France.

3D sequential integration is a promising approach to obtain a vertically stacked FETs (Field Effect Transistors) scheme [1]. This integration offers a very small 3D contact pitch which leads to a wide spectrum of applications like the increase of integration density beyond device scaling [2]. Such an integration requires to limit the thermal budget of top FET processing (T=500°C) [3]. A major challenge is to fabricate high-performance FETs at the top level without electrical characteristic degradation of the bottom active layers.

In order to fulfill the 3D sequential integration requirements, the use of Cu metal lines and ultra low-k dielectric materials between the two FET levels is mandatory. This intermediate Back End Of Line (iBEOL) is still challenging. Indeed, the thermal budget used to process top transistors is far higher than what is usually requested for CMOS interconnects [4], and it can greatly influence material properties and generate defects into the Cu metal lines and in the low-k dielectric.

In this work, the thermal stability of state-of-the-art BEOL structures with four levels of standard Cu/low-k interconnects was evaluated by applying different post-annealing. For this study, experiments were performed on a damascene BEOL integration of state of the art 28 node FDSOI technology on 300 mm wafers [5]. Inter-Metal-Dielectric was composed of 100 nm of porous SiOCH and 20 nm of SiCNH etch stop layer. A SiCNH layer encapsulated the four metal lines/ via levels. Then, different annealing processes (at variable temperatures from 400°C to 600°C) were applied to simulate the thermal budget that the wafers go through during the realization of the top level FETs. Electrical reliability tests on metal 1&2 and on via 1&2 were performed after the removal of the SiCNH encapsulating layer.

The breakdown voltage for line to line and via to line is not significantly modified after a thermal annealing at 500°C for 2h. At higher annealing temperatures, a degradation of the time to breakdown is observed but these modifications cannot be attributed to metal line degradation since no change in the line resistance has been observed. To better understand the mechanisms involved during thermal annealing on the integrated dielectric, the impact of a thermal process on the intrinsic properties of a porous low-k in free surface condition (no capping) was studied. Firstly, constant voltage stress experiments were performed on simple Metal-Insulation-Metal structures with the same low-k as the one used in the four metal levels integration. Secondly, in depth material characterizations such as FTIR, ellipsometry, Electron Spin Resonance were performed. By combining these material data with electrical reliability tests on integrated structures, this work shows that Cu/low-k interconnects can be used in the intermediate BEOL for 3D sequential integration. It brings also a better understanding of the stability and the reliability of these interconnects at temperatures above the classical BEOL one.


9:45 AM BREAK
Metal-organic frameworks (MOFs) are an intriguing class of porous crystalline materials with record internal surface areas. There is tremendous potential for integrating MOFs into microelectronics, e.g., as active sensor coatings or low-k dielectrics.[1] A key enabling step in leveraging the properties of MOFs in microelectronics will be the development of robust thin film deposition methods. Thus far, typical procedures for the deposition of MOF thin films are incompatible with microelectronic fabrication because of corrosion and contamination issues.

We recently demonstrated chemical vapor deposition (CVD) of MOF thin films.[2] The MOF-CVD process allows conformal growth of thin films and extends MOF processing to a range of other quasi-1D van der Waals materials with the goal of identifying the best material for the interconnects. The local temperature measurements have been conducted using micro-Raman spectroscopy in order to determine the behavior near room temperature (f is frequency). However, at low temperature it is dominated by the Lorentzian bulges of the generation–recombination noise at low temperatures, which is unusual for metals. Unexpectedly, the corner frequency of the observed Lorentzian peaks revealed a strong sensitivity to the applied bias. This dependence on electric field was explained by the Frenkel–Poole effect in the scenario where the voltage drop happens predominantly on the defects, which block the quasi-1D conduction channels. We also have investigated electrical characteristics of a range of other quasi-1D materials.


10:45 AM EP07.05.02
Synthesis and Characterization of TaSe2 Nanorods via Facile CVD Processes
Thomas Empante, Ainée Martinez, Michelle Wurch and Ludwig Bartels; University of California, Riverside, Riverside, California, United States.

Transition metal trichalcogenides (TMTs) like that of tantalum triselenide (TaSe2) are of interest due to their low, dimensional, quasi 1D structure and high conductivity. These materials have generally been synthesized using a chemical vapor transport (CVT) process at high temperatures followed by mechanical and/or chemical exfoliation and transferred onto a substrate. Here we present a novel breakthrough in synthesizing these materials through chemical vapor deposition (CVD). The TaSe2 nanorods are synthesized directly onto the desired substrate using relatively low temperatures and under one-hour process times. The obtained results are important for developing the ultimately downscaled local interconnects for future electronic technologies and provides further understanding of the material and its implications for TMTs possible use in future nanometer scale interconnect applications.

11:00 AM EP07.05.03
Current Carrying Capacity and Low-Frequency Noise in Quasi-One-Dimensional Van der Waals Nanowires and Nanoribbons
Adane Geremew1, Ruben Salgado1, Amirmahdi Mohammadzadeh1, Matthew Bloodgood2, Tina Salguero3 and Alexander A. Balandin; University of California, Riverside, Riverside, California, United States; 2Chemistry, University of Georgia, Athens, Georgia, United States; 3Chemistry, University of California, Berkeley, California, United States.

As the aggressive scaling in the complementary metal-oxide semiconductor (CMOS) technology continues, there is a growing need to examine new materials that can be used for nm-scale local interconnects. At present, the current density sustained by Cu interconnects in CMOS technology is between 2 MA/cm2 to 3 MA/cm2. We recently proposed that one quasi-one-dimensional (1D) van der Waals materials, such as transition metal trichalcogenides (TMTs), have properties attractive for applications in nm-scale electronics.[1-2]. In a way similar to transition metal dichalcogenides (TMDs), which exfoliate into 2D layers, TMTs exfoliate, or can be grown into, quasi-1D atomic thread bundles[1-4]. We found that metallic TaSe2 nanoribbons have breakdown current density on the order of ~10 MA/cm2[1]. In principle, such quasi-1D materials could be ultimately downscaled by exfoliation, or grown directly, into nanowires with a cross-section of ~1 nm × 1 nm, which corresponds to an individual atomic thread, i.e. MX2 chain. In this presentation we show that nanoribbons made of ZrTe5, another member of the TMT family, reveal exceptionally high current density, on the order of ~100 MA/cm2, at the peak of the stressing DC current [3]. We have used low-frequency noise (LFN) spectroscopy to investigate carrier recombination in such materials and verify reliability of the van der Waals interconnects [4]. It was found that LFN in ZrTe5 reveals conventional 1/f behavior near room temperature (f is frequency). However, at low temperature it is dominated by the Lorentzian bulges of the generation–recombination noise at low temperatures, which is unusual for metals. Unexpectedly, the corner frequency of the observed Lorentzian peaks revealed a strong sensitivity to the applied bias. This dependence on electric field was explained by the Frenkel–Poole effect in the scenario where the voltage drop happens predominantly on the defects, which block the quasi-1D conduction channels. We also have investigated electrical characteristics of a range of other quasi-1D van der Waals materials with the goal of identifying the best material for the interconnects. The local temperature measurements have been conducted using micro-Raman spectroscopy in order to determine the breakdown mechanism in the quasi-1D van der Waals metallic interconnects. The obtained results are important for developing the ultimately downscaled local interconnects for future electronic technologies.

This work was supported, in part, by the Semiconductor Research Corporation (SRC) contract 2018-NM-2796: One-Dimensional Single-Crystal van-der-Waals Metals: Ultimately-Downscaled Interconnects with Exceptional Current-Carrying Capacity and Reliability, and by the National Science Foundation (NSF) through the Emerging Frontiers of Research Initiative (EFRi) 2-DARE project: Novel Switching Phenomena in Atomic Heterostructures for Multifunctional Applications (NSF EFRi-1433395).


11:15 AM EP07.05.04
Metal Based Self-Healable Electrodes for Foldable Electronics with High Reliability
Minjae Choi, Young-Geun Park, Hyeon Seok An, Jiuk Jang and Jang-Ung Park; Material Science and Engineering, Yonsei University, Seodaemun-gu, Korea (the Republic of).

Self-healable electrodes can improve the durability and the reliability of electronic devices. In recent years, the need of self-healing ability in materials grows in the field of deformable electronics such as foldable or stretchable devices. However, until now, most of developed self-healable electrodes require additional healing agents or several stimuli such as heat, magnetic field, or UV irradiation to restore the electrical conductivity. Also, some of them takes long time to self-heal after being damaged. And, the healing ability of the electrical conductivity is not maintained through only the low number of breaking and healing cycles. Herein, self-healable electrodes based on silver nanoparticles which make up the disadvantages of other self-healable electrodes have been developed. Because the silver makes the main conductive path of the electrodes, the electrical conductivity of the self-healable electrodes is 2×10^4 S/m, which is similar level to other metals. The self-healing phenomenon of electrodes is taken by high-speed camera. If the electrodes are cracked by external forces, they reconnect in 10 milliseconds without any external stimuli or healing agents. The electrodes recover 90% of the initial conductivity during cyclic test of 50 times. Unlike the other metal electrodes, these silver-based electrodes have 60% stretchability. Furthermore, these self-healable electrodes are patterned by photolithography, which can be applied to the conventional fabrication process of electronic circuits. The electrodes are applied to foldable organic light-emitting diodes, maintaining the luminescence after folding the devices.

15:41 AM EP07.05.06
Chemical Vapor Deposition of Nanoporous Metal-Organic Frameworks (MOF-CVD) and Their Integration as Low-k Dielectrics
Rob Ameloot; Center for Surface Chemistry and Catalysis, KU Leuven, Leuven, Belgium.

Metal-organic frameworks (MOFs) are an intriguing class of porous crystalline materials with record internal surface areas. There is tremendous potential for integrating MOFs into microelectronics, e.g., as active sensor coatings or low-k dielectrics.[1] A key enabling step in leveraging the properties of MOFs in microelectronics will be the development of robust thin film deposition methods. Thus far, typical procedures for the deposition of MOF thin films are incompatible with microelectronic fabrication because of corrosion and contamination issues.

We recently demonstrated chemical vapor deposition (CVD) for MOF thin films.[2] The MOF-CVD process allows conformal growth of thin films and extends MOF processing to one of the most commonly used techniques in thin film research and manufacturing. Two important challenges were tackled to realize this process: vapor phase supply of precursors and crystallization at the vapor-solid interface. To our knowledge, this is the first vapor phase process for conformal film deposition of a crystalline and microporous network material. Future directions and potential applications of MOF-CVD coatings will be discussed, with special attention to their integration as low-k dielectrics.

Sputter Deposited Amorphous Carbon for Hard Mask with High Etch Resistance

Young-Chang Joo; Seoul National University, Seoul, Korea (the Republic of).

As the area shrinkage of semiconductor devices with high memory density, the high aspect ratio pattern is needed such as 3D NAND flash. To create a vertical pattern with a mask, mask is needed to be thicker for etching it longer. However, a thick mask distorts the shape of the pattern with a shadowing effect. Therefore, it is necessary to have a hard mask that can be made thinner. The vertical structure is fabricated by plasma based dry etching process with hard masks, which have superior etch resistance. Therefore, it is necessary to study the properties of hard mask materials for deeply patterned devices having higher memory density. The hard mask should have more etch resistant to plasma reactive gas than conventional organic soft mask for deeper patterning. It must also be easily removed after the etching process. These conditions are well satisfied with amorphous carbon, which is the most promising material for hard mask. Amorphous carbon is known that the kind of bonding is changed according to the process conditions. Carbon has various atomic bonds like sp³ of diamond and sp² of graphite. The difference in carbon bond between the two materials greatly affects the properties such as mechanical and electrical properties. In this study, we have studied how the etch characteristics change with the change of bonding nature of amorphous.

Amorphous Carbon (a-C) was deposited on SiO₂/Si by DC magnetron sputter system using graphite solid target for higher purity and lower roughness than CVD process. The deposition pressure and acceleration voltage was controlled to modify the bonding structure of the carbon film, and the bonding was dramatically modified depending on the conditions of pressure, which was an important parameter for the etching characteristics. In case of the low-pressure deposition process, sp³-bonding rich amorphous carbon film was fabricated and had an excellent etching resistance. The other hand, high-pressure deposition process, sp²-bonding rich amorphous carbon film was fabricated and had a poor etching resistance. In order to understand the degradation process of the carbon hardmask induced by the penetration of fluorine ion into the film during dry etching, the phenomenon of fluorine penetration into the film with respect to carbon bonds was proved by density function theory (DFT) calculation. Through the DFT calculation, it is unveiled that the energy barrier for the fluorine atom through sp³ bonding path is much larger than that of the fluorine atom through sp² bonding path in the amorphous carbon.

The doping, which is very well-known process to modify the bonding structure of the carbon film. We fabricate the amorphous carbon film with nitrogen, boron, silicon, and tungsten doping. The effect of the doping elements on the bonding structure of the amorphous carbon film will be discussed.

Wet-Chemical Etching of Ruthenium for Advanced Interconnects

Harold Philipson¹, Nils Mouwen¹, ², Sander Teck¹, ², Wouter Monnens¹, Quoc Toan Le¹, Frank Holsteays¹ and Herbert Struyf²; ¹imec, Leuven, Belgium; ²Technology Campus Groep T, KU Leuven, Leuven, Belgium; ³KU Leuven, Leuven, Belgium.

For damascene metallization, the semiconductor industry uses barrier / liner / seed stacks, such as TaN / Ru / Cu, in which Ru ensures a good adhesion of the Cu seed layer on the TaN barrier, as well as enables ‘reflow’ of the Cu seed to facilitate the Cu filling process by electrochemical deposition (ECD). Next, chemo-mechanical planarization (CMP) is done to achieve metallization which is embedded in a dielectric matrix. Presently, Cu constitutes the largest material fraction as conductor in damascene trenches and is deposited by ECD. In future interconnect technology nodes, Ru is considered a strong candidate to replace Cu, as it shows less electromigration.

Controlled removal of metals is a critical step at many points in a processing flow, such as for bevel cleaning, wafer backside cleaning, and fully aligned vias. For the latter example, a metal recess etch is needed. CMP yields planarized substrates, however, it cannot remove material in a controlled way. For the metal recess etch, the CMP slurries, such as bromate (BrO₃⁻) or periodate (IO₄⁻), are utilized. The etch rate and selectivity of metals such as Ru can be modified by adding oxidizing agents in CMP slurries.

In our contribution, we discuss the (electro)chemistry involved in Ru etching and discuss results for selected oxidizing agents. The etch process is characterized in terms of surface roughness, cleanliness, and etch rate. Solution chemistry as well as stability were characterized using UV-vis spectroscopy. Compatibility with low-k dielectric material was investigated and characterized using Fourier transform infrared spectroscopy.

Oxygen-Assisted Etching of Pt in Supercritical CO₂ Solutions

Eiichi Kondoh; University of Yamanashi, Kofu, Japan.

Platinum has been used as an electrode material in transistors, ferroelectric memories, and recently in magnetic tunnel junction (MTJ) devices. Pt is known as a hard-to-dry etch material due to its nobleness and low volatility of its halides. In past Pt plasma etching, physical sputtering functioned as a dominant etching principle. MTJs have a rather complex thin film stack structure consisting of various metallic layers such as CoFeB, NiFe, MgO, and Co, where MgO is sandwiched with ferromagnetic metals. These ferromagnetic elements (Co, Fe, and Ni) also form low-vapor-pressure chlorides; thus, they should be sputteretched, although sputter etching leads to a deadly sputter residue at the sidewall of a ferromagnetic tunnel junction. Recently atomic layer etching has been gaining a strong attention, whereas the usage of plasma chemistry does not abate its problems. The application of wet chemistry to the residue removal is more problematic owing to its limitation to nanostructures, electrochemical attacks, and etching selectivity.

In the present work, Pt thin films were etched in supercritical CO₂ fluids. Hexafluoroacetylacetone (Hfaca), a fluorinated compound, was added to a supercritical CO₂ fluid together with O₂ at elevated temperatures. Experimental set-up, various process parameter dependences, and Pt oxidation status will be presented.
8:30 AM *EP07.07.01
Electrochemical ALD for Enabling Advanced BEOL Scaling Yezdi Deddi; Lam Research Corporation, Fremont, California, United States.

As BEOL interconnect dimensions continue to shrink, future generation devices will require precise atomic level thickness control for BEOL seed layers. Here, we present the latest developments in interconnect metallization using a new wet process called electrochemical atomic layer deposition (eALD). In this talk, we will discuss innovative modifications to eALD that make this process scalable to full wafers and amenable to the deposition of a variety of metals and alloys. We will review recent success in achieving void-free metallization of sub-20nm interconnect features. We will also explore integration approaches including electroless ALD processing that would enable future interconnect technology nodes.

9:00 AM *EP07.07.02
Approaches to Area Selective Deposition for Next Generation Interconnects Stacey F. Bent; Department of Chemical Engineering, Stanford University, Stanford, California, United States.

Selective deposition is likely to become an important process in pattern fabrication for next-generation interconnects. Bottom-up growth strategies such as selective deposition provide advantages in reduced process complexity and improved pattern fidelity. In this presentation, I will describe different approaches to achieve area selective atomic layer deposition (ALD) for materials systems important to back end of line processing. ALD is a good choice for selective deposition because its chemical specificity provides a means to achieve selectivity on a spatially patterned substrate. One successful approach uses inhibitory layers such as self-assembled monolayers (SAMs) to alter the native surface reactivity, allowing ALD selectivity to be achieved. I will show that this process provides good selectivity for thin deposited films, and demonstrate selective deposition on different materials, including low-k dielectrics and metals such as Cu, Co, W and Ru. Because area selective ALD processes often break down after more than a few nanometers of material is deposited, strategies to overcome the undesired ALD nucleation on the inhibitory layer and achieve significantly higher selectivity in area selective ALD are also important. Two such strategies that improve the final selectivity will be described, including SAM repair between ALD cycles and a self-correcting process in which selective deposition is combined with selective etching. ALD of low-k dielectric thin films as well as selective ALD on low-k dielectric/Cu patterns will also be discussed.

9:30 AM EP07.07.03
Atomic Layer Deposition of Ru for Copper Metallization Anil Mane, Yan Zhang and Jeffrey Elam; Argonne National Laboratory, Lemont, Illinois, United States.

Contact metallization in large-scale semiconductor devices such as logic, memory, MEMS, and SoC using 2.5D and 3D interposers requires a high quality and conductivity metal barrier/seed layer for subsequent metal electroplating. Ruthenium metal has a bulk resistivity of 7.1 μΩ cm, a work function of 4.7 eV, and a low solid solubility with strong adhesion to Cu, making Ru an attractive contact metal barrier metal or seed layer for Cu electroplating. There have been numerous reports of Ru ALD using a variety of precursors. However, technical challenges remain including the need for high growth temperature, very long nucleation delay, and the use of plasma that limits Ru conformality in high aspect ratio features. Currently, there is a strong desire and demand for 3D-devices where high quality, uniform, and conformal metal growth on high aspect ratio structures for ultra largescale integration (ULSI) process flow including for 2.5D and 3D interposer substrates creation.

Here we have developed a low temperature (200°C) Ru atomic layer deposition process using Ru(DMBD)(CO)3 and O2 precursors. To enhance the Ru nucleation and growth, especially at low temperature, we performed low temperature Pt ALD using Pt(MeCp)Me2 and O2 to deposit a sub-monolayer Pt seed layer that greatly accelerates the subsequent Ru nucleation. High quality Ru films were deposited on a variety of substrates including Si(100), fused silica, Al2O3 and TiN. The ALD Ru films were uniform across the 18” deposition zone of our tubular ALD reactor. Thin Ru films were characterized by XPS, SEM, TEM, four point IV measurements, XRD and XRF. We have also performed Cu electroplating on the ALD Ru layers and found that the Ru films deposited using the Pt seed layer exhibited excellent Cu electroplating. Here we will present details of the Ru ALD and Cu electroplating.

9:45 AM BREAK

10:15 AM EP07.07.04
Hyper-Selective Co Metal ALD on Cu and Pt Without Passivation Steven Wolf; Michael Breeden, Scott Ueda and Andrew Kummel; University of California, San Diego, La Jolla, California, United States.

It is desired to have selective metal deposition for bottom-up fill for both middle-of-line (MOL or MEL) and back-end-of-line (BEOL) processing. This would induce formation and growth of larger grains, which are expected to decrease via and interconnect resistance by reducing grain boundaries and decreasing surface roughness. In addition, bottom-up growth may remove the need for nucleation layers on low-k dielectrics (SiCOH) since the nucleation will occur only on the bottom surface. The key metals for bottom-up growth include cobalt and ruthenium; cobalt is particularly important since it was used as both a capping layer on Cu to protect it from oxidation, and in sub 10 nm vias, where Co is considered to be a better conductor than Cu due to Co having a smaller electron mean free path and problems with Cu electroplating in sub 10 nm vias.

ALD cobalt metal was explored using a metal-organic cobalt precursor, Bis(1,4-di-tert-butyl-1,3-diazadienyl) cobalt (Co(dad)), and either a co-reactant of formic acid (HCOOH) or tert-butylamine (TBA) at 180°C on Cu, Pt, and SiO2 substrates. The deposited Co films were studied using in-situ x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Cross-sectional scanning electron microscopy (SEM) and 4-point probe measurements were performed to check film thickness and resistivity, respectively.

It was found that there is nearly infinite selective deposition of Co on a conductor and not an SiO2 for 180°C ALD with Co(dad); and HCOOH. XPS was performed after 100 ALD cycles followed by an additional 100 cycles on UHV annealed Pt vs SiO2. On Pt, a thick (~10 nm) CoxOy film deposits while virtually no deposition results on SiO2. AFM images show no change on SiO2 before and after Co ALD cycles consistent with no nuclei formation, while the Co on Pt surface roughness remains below 1.8 nm. To verify self-limiting precursor exposures consistent with ALD, a saturation study was performed and monitored with XPS; this study highlighted the effect of individual additional half cycle amounts that result in self-limiting Co(dad), and HCOOH exposures consistent with ALD. Additionally, this study revealed a novel mechanism about the reaction. Previously it was thought the HCOOH dissociatively chemisorbed to produce atomic H which removed the ligands from Co(dad). Instead, XPS showed that HCOOH did not remove the ligands but instead induced a ligand-exchange process. The Co 2p peak indicated the HCOOH leaves a higher binding energy component on the surface consistent with a formate on the surface.

Deposition with HCOOH was attempted on Cu substrates; however, the substrate Cu signal never decreased to zero consistent with etching by HCOOH so an alkyl amine co-reactant (TBA) was also studied. For Co(dad) + TBA ALD at 180°C, reduced Co metal films were deposited on Cu and Pt substrates with hyper-selectivity against SiO2. Films as thick as 30 nm were grown on the conductors without etching the substrates. On SiO2, only 4% CoOx, was deposited after an initial 50 ALD cycles. After an additional 250 ALD cycles, there was still only 4% CoOx, consistent with saturation and hyper-selectivity. AFM imaging from ALD with TBA confirmed low surface roughness ALD on Pt and Cu, while only small (~5 nm) CoOx particles were present on SiO2.

Hyper-selective Co metal deposition was produced from Co(dad); and both co-reactants (HCOOH and TBA). Utilizing HCOOH, no deposition was seen on SiO2 consistent with infinite deposition, however HCOOH was observed to etch Cu. By switching to TBA, no Cu etching was observed and similar metallic Co films were deposited with only 4% CoOx, on SiO2, independent of the number of Co ALD cycles. The self-limiting deposition on SiO2 is a novel mechanism of selectivity through the formation of an oxide particulate, which results in hyper-selectivity.

10:30 AM EP07.07.05
As have been widely known, The NAND Flash business is transitioning from the conventional two dimensional, planar structure to three dimensional (3D), vertical structures to meet storage density requirements. Also, in 3D V-NAND Flash memory devices, and device scaling has been achieved by vertical stacking of thin film transistors (TFTs) in multiple layer configurations, without heavily relying on advances in lithography. 3D V-NAND Flash memory device fabrication involves many processes that have never before been used in mass production of semiconductor devices, and are extraordinarily challenging. Precise control of every process step is required.

Thickness reduction of 3D Channel layers is a very challenging issue due to the scale-down, vertical etch, and gapfill process limitation of devices. For overcoming these issues, Alternate deposition of ultra-thin films and selective etching are required for successful fabrication of vertically stacked layers used in 3D V-NAND Flash memory devices. In particular, after it has formed a vertical gate channel by the multiple Oxide-Nitride (ON) stack layers, and the gapfill process for gate isolation is switching from the existing Chemical Vapor Deposition (CVD) Type deposition process to the new Atomic Layer Deposition (ALD) type.

In general, the ALD process has known as the most stable and effective process in the gapfill process up to now by controlling the atomic-layer depositions by the precursor and the source loading time. However, in the gapfill process of 3D NAND flash device with an over 50th floors, as the number of stacked layers increases, the area to gapfill increases proportionally. And ALD process has encountered other new huddles for stable processes. Those are the characteristic deference of gapfill material in the top/bottom area, the void by overhang increasing in top area, and the re-spattering phenomenon by ion bombardment in bottom area. Finally, these unstable ALD processes has triggered a metal bridge to cause an electronic leakage, and the degradation of device characteristic in Word Line (WL) block fail by channel threshold voltage(Vt) drop.

ALD process has evaluated in process parameter optimization to improve deposition conformality by the controls in source gas compositions, source/co-gas partial pressure, RF power or RF process time, burst pulse flow ratio, and chamber press. However, the evaluations to improve the step coverage of the ALD layer has been improved results by dropping the deposition ratio. In other words, to improve the conformality of ALD Layer has been unavoidable to lose the production efficiency. The enforcement of source gas plasma density could make the material characteristics of ALD layer stable but the conformality severe weaken.

In this study, we have evaluated the shape change possibility of as-deposited ALD layer and the strengthening the ALD layer by optimizing the post treatment. We have measured with high resolution cross-sectional transmission electron microscopy (HRXTEM) in real patterned wafer for the ALD layer conformality transition trace by post treatment ALD Layer Thickness. And then, we have evaluated Wet Etch Rate (WER) in 300:1 HF diluted solution for the ALD layer densification trace. We have demonstrated the possibility of ALD Shape and material characteristics improvement. And we have evaluated the possibility of post treatment of high temperature ALD without loss in production efficiency as like Units Per Hour (UPH).

10:45 AM EP07.07.06
Surface Engineering by Plasma and Organic Films to Enable Area Selective Deposition in BEOL Silvia Armini, Ivan Zyulkov and Mattia Pasquali; imec, Leuven, Belgium.

Integrating bottom-up area-selective building-blocks in microelectronics has a disruptive potential because of the unique capability of engineering new structures and architectures. Atomic layer deposition (ALD) is an enabling technology, yet understanding the surfaces and their modification is crucial to leverage area-selective ALD (AS-ALD) in this field. The understanding of general selectivity mechanisms and the compatibility of plasma surface modifications with existing materials and processes, both at research and production scale, will greatly facilitate AS-ALD integration in microelectronics. The use of self-assembled monolayers to inhibit the nucleation and growth of ALD films is an alternative route to bottom-up area-selective nanofabrication. In our work, we demonstrate i) a straightforward plasma surface modification process capable of inhibiting Ru ALD nucleation on an amorphous carbon surface while still allowing instantaneous nucleation and linear growth on Si-containing materials; ii) metal and/or dielectric surface passivation by molecular organic films which enable AS-ALD of dielectric materials on dielectric surfaces and/or AS-ALD of metallic films on metal surface. Demonstration of ASD on patterned critical dimensions below 50 nm and applications of ASD in back-end-of-line (BEOL) will be illustrated.

11:00 AM EP07.07.07
Electrochemical Nanoimprinting of 3D Hierarchical Micro- and Nano-Structures in Silicon Bruno Azeredo1, Aliaksandr Sharstniou1 and Stanislau Niauznour2; 1 Arizona State University, Mesa, Arizona, United States; 2 Belarusian State University, Minsk, Belarus.

Freeform 3D single-crystal silicon micro- and nanostructures offer the opportunity to topologically define the refractive index of a medium. In turn, they enable realization of a myriad of optical devices such as classical elements, metasurface-based elements for silicon photonics, x-ray flat-lenses, optical resonators for biosensing, biomimetic lenses & imagers, and graded-index materials for photovoltaics and space applications. However, existing parallel bulk micromaching processes for silicon do not offer the ability to fabricate freeform structures with specific challenges when it comes to hierarchical micro and nanoscale 3D features, particularly during reactive etching, which in turn limits resolution, aspect-ratio and surface roughness. This paper demonstrates an electrochemical nanoimprinting process for single-crystal semiconductors for directly etching 3D features into silicon wafers. It is shown that stamps made of porous catalysts play a critical role in enabling diffusion of chemical species during imprinting which, in turn, allows for morphology control of imprinted silicon features with sub-20 nm resolution in 3D. This process delivers mirror surface finish (RMS < 5 nm), low-defect density, and large-area patterning (>1 cm²) in a single imprinting operation. Further, it outperforms the resolution and scalability of leading serial (e.g. FIB, electron beam) and parallel (e.g. gray-scale lithography) methods altogether by an order of magnitude, allowing for fast replication of patterns onto hard materials from a soft mold. This technique bypasses the need for dry etching and is potentially compatible with roll-to-roll platforms, amorphous and poly silicon and III-V semiconductors. In turn, it may pave the way for the manufacturing of complex objects for infrared optics.

SYMPOSIUM EP08

Phase-Change Materials for Memories, Photonics, Neuromorphic and Emerging Application
April 23 - April 25, 2019

Symposium Organizers
Marie-Claire Cyrille, CEA - LETI
Paolo Fantini, Micron Technology Inc.
Juejun Hu, Massachusetts Institute of Technology
Kotaro Makino, National Institute of Advanced Industrial Science and Technology (AIST)

* Invited Paper

SESSION EP08.01: Characterization of Phase Change Materials
Session Chair: Robert Simpson
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 222 B

10:30 AM EP08.01.01
Nanosecond Resolved Probing of Single Silicon Nanostructure Reversible Phase Change Letian Wang1, Heng Pan2 and Costas Grigoropoulos1; 1University of California, Berkeley, Berkeley, California, United States; 2Missouri University of Science and Technology, Rolla, Missouri, United States.

On-demand phase transformation of silicon is of great technical importance for electronics, MEMES and photonics. While numerous efforts have been made towards
understanding the phase change of thin films, scientific knowledge is limited in nanoscale phase transformation.

Here we probed the nanosecond resolved crystallization and amorphization dynamics of a single silicon nanostructure with 200nm diameter. Based on the Mie resonance and thermo-optic effect, we successfully identified the heating, melting, deformation, solidification and cooling states during the phase transformations. The results revealed the superlateral crystallization of 2ns time scale and amorphization of 10ns. Combined with comprehensive heat-transfer and Monte Carlo based nucleation and phase change simulation, the study offered significant insights into the different super-coolings, cooling rates and corresponded mechanisms of crystallization and amorphization.

Materials with rationally controlled properties play important parts in the development of new and advanced technologies. For instance, the thermoelectric, phase-change, or topologically insulating materials can be traced back, to a significant extent, to the nature of bonding in materials. Here, we develop a two-dimensional map based on a quantum-topological description of electron sharing and electron transfer. This map intuitively identifies the fundamental nature of ionic, metallic, and covalent bonding in a range of elements and binary materials. Furthermore, it highlights a distinct region for a mechanism recently termed “metavalent” bonding. Extending this map into the third dimension by including physical properties of application interest, we show that bonding in metavalent compounds differs from the classical textbooks views of bonding. This map could be used to help designing new materials: by searching for desired properties in a 3D space and then mapping this back onto the 2D plane of bonding.

11:00 AM *EP08.01.03
Multiferroics in Interfacial Phase-Change Memory Junji Tominaga; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

It is almost ten years since interfacial phase-change memory (iPCM) was developed. Although iPCM was originally designed to save switching energy of phase-change memory (PCM) by reducing entropy energy loss at the phase transition as small as possible, it was found later that the layered structures may provide a good platform to study topological insulators and related semimetals (Dirac and Weyl). The topological properties of iPCM rely on the crystalline structures, which satisfy or not the spatial inversion symmetry. If the iPCM has the symmetry, magnetic properties are not induced because the electronic band structures are degenerated. This is the case for Kool, Petrov and inverted-Petrov phases. On the other hand, the only ferroelectric phase of iPCM breaks the symmetry, which lifts two different spin bands, resulting in magnetized. Interestingly, the magnetic properties attribute to p-electrons in Ge, Sb and Te, which are all non-magnetic elements.

Multiferroics is a keyword for future electronics as well as topological insulator. However, it is still difficult to induce large electrical and magnetic properties at room temperature. It relies on that electric dipole moments are usually related to p-electrons while the magnetic moments are to d-electrons. If a large magnetic moment is induced from p-electrons, a giant multiferroics would be possible. A combination of a topological insulator and a ferroelectric insulator may open a new era to realize such the multifunctionality. Topological insulators, such as Bi$_2$Te$_3$ and Sb$_2$Te$_3$, usually satisfy both spatial inversion and time reversal symmetry. The topological surface bands are mainly made of the band inversion of 6p- or 5p-electrons of Te, Sb and Bi. On the other hand, GeTe is known as a ferroelectric material, which has a large spin-orbit coupling (SOC) compared with other oxide ferroelectric materials. Due to the large SOC, it shows a large Rashba-like spin split bands. It is noted here that the existence of an electric dipole moment breaks the spatial inversion symmetry. If thin films of Sb$_2$Te$_3$ and GeTe are piled up alternatively, what happens on the band structure as the bulk film? Actually, both layers can share a lattice plane using (0001) and (111) through van der Waals force. As the bulk film, the spatial inversion symmetry is broken. Therefore, plural Dirac cones appear apart from the Γ-point in the k-space, resulting in a Weyl semimetal. Weyl semimetals are magnetic sensitive because spin bands are lifted from the band degenerations.

In the presentation, we show several experimental results of the Weyl semimetal from superlattices consisted of GeTe and Sb$_2$Te$_3$ sublayers at room temperature.

References:

11:30 AM *EP08.01.04
Phase Change Materials Probed by Angularly Resolved Photoelectron Spectroscopy and Scanning Tunneling Spectroscopy Markus Morgenstern; Institute of Physics B, RWTH Aachen University, Aachen, Germany.

Epitaxially grown GeSbTe alloys in the metastable rock-salt phase and the stable trigonal phase are transferred in ultrahigh vacuum to employ angularly resolved photoelectron spectroscopy (ARPES) and scanning tunneling spectroscopy (STS). Firstly, we map the band structure of Ge$_2$Sb$_2$Te$_5$ [1] within the whole Brillouin zone, which exhibits valence band maxima away from the G point and well below the Fermi level. Hence, the Fermi level is pinned in the disorder broadened part of the bands constituting a so-called pseudo-Fermi-surface, where each enclosed state contributes only partially to the conductivity. The resulting hole density of this pseudo Fermi-surface agrees well with results from Hall measurements of the same sample type.

Moreover, via two-photon ARPES, we found an in-gap surface state with largely linear dispersion and a circular dichroism being mirror symmetric in k-space as expected for a topological surface state. Estimates, however, showed that the intrinsic bulk carrier density overwhelms the charge carrier density from this surface state significantly, such that the surface state is likely not relevant for the transport properties of metastable Ge$_2$Sb$_2$Te$_5$.

Using STS, we established methods to probe the subsurface GeSb layer, which includes vacancies and is located below the covering Te layer [2]. It turns out that the subsurface layer is relatively ordered such that individual defects can be spotted. Finally, we contact the GeSbTe layers with the STM tip and are able to switch the resulting circuit between states of different conductivity via applying voltages of about 1V.

existing tuning mechanisms are slow and volatile. In contrast, phase change materials (PCMs) offer non-volatile programmability on sub-nanosecond time scales. Unfortunately the common phase change materials, which were originally developed for data storage, strongly absorb visible light and tend to exhibit a relatively small change to the real part of the refractive index, \( \Delta \Re(n) \), in the visible spectrum. A large \( \Delta \Re(n) \) is required to tune the resonant frequency of photonics structures. Therefore, new phase change materials that exhibit a large \( \Delta \Re(n) \) must be designed specifically to transmit visible light.

Antimony sulphide (Sb\(_2\)S\(_3\)) is a somewhat misunderstood PCM. It exhibits a large \( \Delta \Re(n) \) between its amorphous and crystalline phases\(^1\) and transmits visible light. It was originally explored in the 1990s for data storage applications but was soon forgotten because it seemed difficult to amorphise using laser pulses\(^2\). At the time PCMs were being developed for rewritable compact discs (CDs) and digital versatile discs (DVDs), which operated at wavelengths of 780 nm and 658 nm respectively. The large band gap of Sb\(_2\)S\(_3\) prevented it from efficiently absorbing the laser energy, which is required to heat the material and induce structural phase transitions. However, recently we designed resonator structures that strongly enhance the absorption of Sb\(_2\)S\(_3\) and in turn allow it to be efficiently heated and subsequently amorphised on a nanosecond time scale using laser pulses\(^1\).

We have now applied Sb\(_2\)S\(_3\) to a variety of different optical resonator structures, which allow control of both the intensity and phase of the transmitted light. In this talk, the properties of Sb\(_2\)S\(_3\) will be presented, and the performance of our latest reprogrammable visible photonics devices will be discussed.


2:00 PM **EP08.02.02**

**Gradient Integrated Silicon Photonics**

Jiajiu Zheng\(^1\), Amey Khandojar\(^2\), Peipeng Xu\(^1,\(^3\), Shane Colburn\(^1\), Sanchit Deshmukh\(^1\), Jason Myers\(^1\), Jesse Frantz\(^2\), Eric Pop\(^1\), Joshua Hendrickson\(^1\), Jonathan Doyyland\(^1\), Nicholas Boechler\(^1\) and Arka Majumdar\(^1,\(^2\)).

Department of Electrical Engineering, University of Washington, Seattle, Washington, United States; Department of Mechanical Engineering, University of Washington, Seattle, Washington, United States; Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province, Ningbo University, Ningbo, China; Department of Electrical Engineering, Stanford University, Stanford, California, United States; U.S. Naval Research Laboratory, Washington, District of Columbia, United States; Sensors Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, Ohio, United States; Silicon Photonic Products Division, Intel Corporation, Santa Clara, California, United States; Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California, United States; Department of Physics, University of Washington, Seattle, Washington, United States.

Reconfiguration of silicon photonic integrated circuits relying on the weak, volatile thermo-optic or electro-optic effect of silicon usually suffers from large footprint and energy consumption. Here, integrating a phase-change material, Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) with silicon microring resonators, we demonstrate an energy-efficient, compact, non-volatile, reprogrammable platform. By adjusting the energy and number of free-space laser pulses applied to the GST, we characterize the strong broadband attenuation and optical phase modulation effects of the platform, and perform quasi-continuous tuning enabled by the thermo-optically-induced phase changes. As a result, a non-volatile optical switch with high extinction ratio as large as 33 dB is demonstrated. We also demonstrated new device design to demonstrate low loss directional coupler, even though the material itself has very low loss. Finally, using thermal heater based on silicon p-i-n junction, we demonstrated electrical actuation of the phase transition. Few cycles of switching were demonstrated.

2:30 PM **EP08.02.03**

**Photonic Computing Using Non-von Neumann and Neuromorphic Techniques and Phase Change Materials**

Harish Bhaskaran (Department of Materials, University of Oxford, Oxford, United Kingdom).

In this talk, I shall cover recent developments in the field of evanescently couple phase change materials-based photonic devices. Specifically, the use of such devices to carry out non-von Neumann computing approaches, where processing and memory can be co-located, but on integrated photonic chips will be the primary topic. Specific examples related to matrix-vector multiplications as well as scaling up these techniques towards larger matrices, carrying out electro-optical conversions and reducing power and wafer real estate requirements will also be discussed.

3:00 PM BREAK

**SESSION EP08.03: Photonics Applications of Phase Change Materials**

Chair: Harish Bhaskaran, Robert Simpson (Tuesday Afternoon, April 23, 2019)

3:30 PM **EP08.03.01**

**Gradient Index (GRIN) Optics for Next Generation EO/IR Sensors**

Clark R. Baleine\(^1,\(^2\), Andrew Kirk\(^1\), Brandon Tripplett\(^1\), Johann Veras\(^1\), Erwan Baleine\(^1\), Kathleen Richardson\(^1\), Myungkog Kang\(^2\), Cesar Blanco\(^1\), Tian Gu\(^1\), Mikhail Y. Shalaginov\(^1\), Yifei Zhang\(^1\), Ray Hilton\(^1\), Tom Loretz\(^4\), Alexej Pogrebnyakov\(^4\), Andrew Swisher\(^4\) and Theresa Mayer\(^6\), Luke Bleen\(^1\), R. Lockhead Martin, Orlando, Florida, United States; University of Central Florida, Orlando, Florida, United States; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; Amorphous Materials Inc., Garland, Texas, United States; The Pennsylvania State University, State College, Pennsylvania, United States; Virginia Tech, Blacksburg, Virginia, United States.

The number of broadband infrared (IR) materials that are commercially available is very limited. This in turn limits the design of current Electro-Optical / Infrared (EO/IR) sensors; making them bulky and expensive to manufacture. However, next generation EO/IR sensors, will require more compact, lighter and cost-effective systems for applications where size, weight, power and cost (SWaP-C) becomes a limitation. Due to this fact, the design of next generation EO/IR sensors will require novel multi-functional materials, with tailorable optical properties that can be engineered to serve complex optical functions. In this work, we highlight the development of broadband IR materials including chalcogenide glass-ceramics and chalcogenide phase change materials with tailorable optical properties. The local refractive index of the material is modified by controlling the local concentration of nanocrystals in the glass matrix using a laser; thus, facilitating the fabrication of complex gradient index (GRIN) components. In this work, we exploit this additional degree of freedom, not available in traditional IR materials, to develop more compact optical designs to enable next generation EO/IR sensors for SWaP-C limited applications.

We demonstrate the imaging power of our broadband GRIN materials by designing, fabricating and characterizing a flat GRIN lens. Typically, 1-in diameter coupons are readily fabricated. The progress in manufacturing readiness level (MRL) will also be discussed. Finally, the properties of novel broadband phase change materials will be highlighted. This material exhibits a large refractive index dispersion, in the order of 1.5, across the IR spectrum. The design, fabrication and characterization of reconfigurable flat metasurfaces will also be presented.

4:00 PM **EP08.03.02**

**Chalcogenide Phase-Change Photonic Metamaterials**

Behrad Gholipour\(^5\), Davide Piccinotti\(^1\), Artemios Karvounis\(^1\), Tiago Martins\(^4,\(^5\), Kevin F. MacDonald\(^1\) and Nikolay Zheludev\(^6\).

University of Porto, Porto, Portugal; Nanyang Technological University, Singapore, Singapore.
Chalcogenide semiconductor alloys offer a uniquely functional and compositionally-controllable material base for nanophotonic, plasmonic and optical-frequency metamaterial applications. They variously present high- and low-index dielectric, low-epsilon and plasmonic properties at near-UV to near-IR wavelengths, coupled to a capacity for fast, non-volatile, electrically–optically-induced switching between phase states with markedly different properties. We present recent developments in their application to non-volatile reconfiguration in photonic metamaterials, including: switchable ‘structural colors’ underpinned by a transition between characteristically dielectric and plasmonic states; and the first optically-switchable UV/HEV dielectric metamaterials, wherein the functional chalcogenide is hybridized with a transparent, high-index dielectric supporting the resonant mode and phase-switching, unusually, changes resonance quality but not spectral position.

4:30 PM EP08.03.03
The Development and Application of Tunable Phase-Change Band-Pass Filters Liam Trimby, David Wright and Anna Bal'dycheva; University of Exeter, Exeter, United Kingdom.

A periodic array of sub-wavelength apertures in a thin metal film exhibits high transmission (transparency) for a narrow wavelength band, with the majority of light otherwise reflected, a phenomenon known as extraordinary optical transmission (EOT) [1]. In this work, such a hole-array is coated in a phase-change material (PCM), specifically Ge$_2$Sb$_2$Te$_5$ or Ge$_2$Sb$_2$Te$_6$, whose refractive index changes the wavelength at which incident light can couple into the metallic hole-array. Since the refractive index of the PCM can be altered by changing its phase-state, the PCM layer enables the EOT transmission peak to be dynamically tuned (shifted) in wavelength, so providing the functionality of a tunable band-pass filter [2]. Moreover, such filters can work in almost any wavelength range for which a suitably low-loss PCM is available. Here we show filtering operation in the 3 to 5 µm and 8 to 12 µm infrared wavebands. Since such filters are ultra-thin, solid-state and can be continuously tuned, they are suited to multispectral imaging and display applications. They also possess large field enhancements within the holes, opening up the possibility for use as chemical sensors with enhanced sensitivity. Many advantages of phase-change materials in general transfer to these filters, namely fast (ns) nonvolatile (years) switching, with excellent cycling endurance [3]. It is also possible to add or remove additional characteristics to these filters, such as polarization or angular sensitivity, by carefully selecting the shape of the holes used to pattern the metallic layer [4].

For multispectral imaging applications, the PCM band-pass filter is placed in the optical path between a scene and a high-speed camera. Multiple images are then taken as the center wavelength of the filter is scanned continuously over the waveband of interest by progressively crystallizing the PCM layer. The advantages of this method are the wide wavelength range applicability, and that spectral resolution can be improved using a higher speed camera or tuning the filter less rapidly (by lowering the temperature used for crystallization of the PCM layer).

Another possible application that we explore is the provision auto-referencing chemical sensors that utilize infrared absorption spectroscopy for analyte identification. Here the filter’s resonance wavelength is designed to match the primary absorption peak of the analyte. The high field enhancement within the filter’s hole-array causes strong absorption at what would normally be the high transmission wavelength, so yielding high measurement sensitivity. The filter can then be tuned to a region in which the analyte does not absorb, and a baseline taken to allow for auto-referencing.

Finally, we consider a third potential application, that of infrared displays. Here, by layering one filter on top of another we can control both the transmission wavelength and the transmitted intensity. Such a configuration could thus be combined with a broad-band infrared source to produce sub-wavelength thick, kHz refresh rate, infrared displays capable of producing almost any arbitrary test image (e.g. for sensor calibration, target identification etc.).

References

4:45 PM EP08.03.04
Terahertz Spectroscopic Characterization of Ge$_2$Sb$_2$Te$_5$ Phase Change Materials Kotaro Makino$^1$, Kosaku Kato$^2$, Yuta Saito$^3$, Paul Fons$^4$, Alexander Kolobov$^{1, 3}$, Junji Tominaga$^1$, Takashi Nakano$^2$ and Makoto Nakajima$^3$; 1National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 2Institute of Laser Engineering (ILE), Osaka University, Suita, Japan; 3Department of Physical Electronics, Herzen University, St. Petersburg, Russian Federation.

Ge-Sb-Te (GST) phase change materials exhibit a structural phase transition between amorphous and two crystalline phases. With increase in temperature, amorphous GST transforms into cubic and hexagonal crystals at around 150 °C and 350 °C, respectively. During this phase change process, not only optical reflectivity, but also carrier density and mobility significantly enhance. Based on these properties, various kinds of new optical and electrical applications, such as optical memory/logic, display, and RF switch, have been proposed. However, optical properties in the terahertz (THz) frequency region have not been fully unveiled, although GST is expected to be utilized for THz optoelectronic device applications [1]. In this study, we employed a transmission-type THz time-domain spectroscopy (THz-TDS) and evaluated the optical properties of GST thin films in the THz frequency range. The samples were Ge$_2$Sb$_2$Te$_5$ alloy films (100 nm) deposited on Al$_2$O$_3$ substrates. Zr$_2$Si$_2$O$_7$ protection layers (20 nm) were then deposited. The GST film was grown at room temperature and then annealed at 150 – 400 °C for an hour to obtain crystalline GST films. It was found that the absorption coefficient increases over the entire frequency range of the measurement (0.2 ~ 2.5 THz) with increase in the annealing temperature. The obtained flat transmittance curves are a characteristic of Drude absorption and indicate that the temperature and then annealed at 150 ~ 400 °C for an hour to obtain crystalline GST films. It was found that the absorption coefficient increases over the entire frequency range of

We present the highly ordered array of vanadium dioxide (VO$_2$) nanodots using nanoporous templates fabricated by block copolymers-based lithography. Thin layers of poly(vinyl alcohol) (PVA) and polystyrene-block-poly(2-vinyl pyridine) (S2VP) are subsequently prepared on a silicon (Si), glass, and sapphire (Al$_2$O$_3$) substrate by spin-coating method. Then, the S2VP thin film on the PVA layer is solvent-annealed in toluene vapor for inducing its self-assembly, so that hexagonally packed poly(2-vinyl pyridine) (P2VP) cylinders oriented vertically to the surface are achieved. After the S2VP thin film is immersed in ethanol which is a selective solvent of P2VP blocks, the resulting film shows hexagonally packed nanoporous structures on its surface. Subsequently, the layer of VO$_2$ is uniformly deposited on nanoporous templates using vanadium (V) target with magnetron sputtering system. As the underlying PVA template as a sacrificial layer is removed by washing with water, only hexagonal array of VO$_2$ dots is remained on the surface. Since VO$_2$ is a phase-change material driven by temperature, electrical properties of these VO$_2$ dots are characterized by varying temperatures.
Much attention has been paid to next-generation memory devices capable of low-power consumption and high-density integration. We have recently reported a novel nonvolatile memory device (Voltage switching Random Access Memory: VolRAM) based on the change in the standard electrode potential. The advantage of this device is the low-power consumption, however, the relation between the applied pulses voltages for switching and power consumption remains unclear. Accordingly, we studied memory operations using pulsed voltages, regarding power consumption.

The device consists of a stack of Li, Li$_2$PO$_4$ solid electrolyte, and Ni thin films on glass substrate. All the processes including fabrication and evaluation were performed without exposing samples to air using our custom-made system. We first fabricated VolRAM devices with a stacked structure of Li(1 µm)/Li$_2$PO$_4$(1 µm)/Ni(100 nm) on glass substrates, with a typical diameter of 0.5 mm. For VolRAM operation, we applied rectangular wave pulsed voltages (maximum of 4.5 V vs. Li) between Ni-Li electrodes as the initial state with an open-circuit voltage of 0.95 V (Low-voltage state). Both of the pulse-width and waiting time between each pulse were set to 100 ms. The amount of Li migration during voltage application was calculated by the time integration of current observed in the circuit. After applying the pulsed voltages, the time dependence of the open-circuit voltage was measured.

The open-circuit voltage increased as the number of application pulses increased. The voltage states of VolRAM successfully switched from low-voltage state to intermediate- and high-voltage state by the applications with 2 and 20 pulses, respectively. Note that the amount of Li ions migrating in the two pulses was 26.1 pC/µm$^2$. If we assume this device to be the size of 20 nm × 20 nm, the power required for switching is 5 × 10$^{-14}$ J. This value is very small compared with the typical energy required by a DRAM device: 10$^{-13}$ J. Thus, we succeeded in the operation of VolRAM by applying pulsed voltages with very low power consumption.

References
tension etc.). Post-printing processing of the thin films involves sintering/curing which could need high temperature and must be optimized for not only different printing methods but also for different inks and specific applications. As 3D printing can create arbitrary structures, it will be invaluable if the technology can be applied to print optical waveguides, gratings or oscillators. To take a step towards this, we report a step-by-step process for inkjet printing of chalcogenide glass starting from glass synthesis. Chalcogenide glasses (ChGs) are phase change materials that are widely used in optical and electrical memory because of their high refractive index, transparency in infrared (IR) region, high resistivity contrast between two phases and thermally driven amorphous-to-crystalline phase change. As an amorphous material, they have a remarkable tolerance to impurities, compositional variance and radiation-induced damage. Their phase transition to a crystalline condition caused high interest due to the application in the electronic or optical recording. While this requires development and synthesis of low-temperature switching mechanisms, recent advancements in ChGs application as temperature sensors in nuclear facilities demand glasses with high crystallization temperature ($T_c$) and high refractive index ($n$). High coordination number and relatively strong chemical bonds of Ge containing binary ChGs make them promising candidates in that aspect. The printing process starts with glass synthesis and then nanoparticles (diameter $\leq$ 100 nm) are obtained by an optimized wet milling of the bulk glass followed by ultrasonication. Cylcocode is used to suspend the nanoparticles and to avoid agglomeration, ethyl cellulose is added as a surfactant. Once the particle size and viscosity (2-30 cP for Dimatix) are characterized by a DLS system and a Rheometer respectively, the ink is used in a Dimatix inkjet printer to obtain printed thin films. Printing requires optimization of the ink parameters, as well as the piezoelectric nozzle controlling performance. Development of these specific parameters and the sintering process optimization for obtaining of homogeneous thin films are described in details and discussed based on the ChG glasses composition. Reflective indices and extinction coefficients of the thin films were measured as the films were produced and after heating at various target temperatures up to their crystallization temperature directly in a hot stage in an ellipsometer using light of 270 nm to 1650 nm. The surface morphology of the films was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

**EP08.04.06** Vis-NIR Responsive Metal-Insulator Transition in Ag-Decorated VO$_2$ Nanorod Arrays **Kookun Hong, Jun Min Suh, Seokhoon Choi and Ho Won Jang**; Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Metal-insulator transition (MIT) in strongly correlated materials has enormous potential with scientific and technological impacts in future oxide nanoelectronic devices. While photo-driven MIT can provide opportunities to extend the novel functionality of strongly correlated materials, there have rarely been reports on it. Here we report MIT provoked by visible-near infrared (Vis-NIR) light in Ag-decorated VO$_2$ nanorod arrays (NRs) due to localized surface plasmon resonance (LSPR). Under Vis-NIR illumination, strong electric fields, generated at the interface between Ag nanoparticles and VO$_2$ NRs by LSPR, affect the electronic state of VO$_2$ and provoke MIT and structural phase transition in VO$_2$ NRs. Due to LSPR-induced MIT in VO$_2$ under Vis-NIR illumination, Ag-decorated VO$_2$ NRs exhibit MIT-driven broad spectral response with high and fast response. Our study will open up the new strategy to trigger MIT, a new functionalization in strongly correlated materials and serves as a valuable proof-of-concept for next generation optoelectronic devices with fast switching speed, large optical band gap and large refractive index change. We have shown that by using Sb$_2$S$_3$ in a simple optical resonator, the resonant frequency can be manipulated without the need of phase change materials. The fundamental resonance change can be inferred.

**EP08.04.07** Pump-Probe Approach to Optical Phase Change Material Characterization **Gary Sevison,** $^1$-2, Joshua A. Burrow$^1$, Pengfei Guo$^1$, Andrew Sarangan$^1$, Joshua Hendrickson$^1$ and Inaad Aguil$^1$,$^3$; $^1$Electro-Optics, University of Dayton, Dayton, Ohio, United States; $^2$Air Force Research Laboratory, Dayton, Ohio, United States; $^3$Physics, University of Dayton, Dayton, Ohio, United States.

Phase change materials (PCMs) are currently being explored for use in a number of photonics applications due to their interesting characteristics. These materials have the ability to switch to multiple different states in a non-volatile fashion. These states can have drastically different optical characteristics. By controlling the state of the material, the amplitude and phase of light passing through or reflected off the material can be controlled. This can lead to the creation of many different photonic devices including high-speed light modulators and optical memories. We characterize the temporal dynamics and quantity of crystalization of GeSb$_2$Te$_5$ (GST) utilizing a pump-probe setup. The pulses to facilitate the switching are created via a CW 1550 nm NP Photonics laser, an arbitrary waveform generator (AWG), and an electro-optic modulator (EOM). The pulses are then amplified by an erbium doped fiber amplifier (EDFA). Post EDFA, the probe laser (a 1580 nm CW Agilent laser amplified by a second EDFA) is coupled into the same fiber using an 80/20 fiber splitter. The probe power needs to be low enough that there is not extra heating of the sample, which would affect the phase change characteristics, but high enough to be detectable after reflection. The resulting mixed signal is then passed through a free-space EOM (used to pick off an arbitrary number of pulses) and coalesced with a 780 nm laser that is used for visually positioning the pump and probe lasers on the sample. The light then is sent into a microscope where it is incident on the GST on silicon sample. The reflected light is coupled back into a fiber and passes through two wavelength division multiplexers (WDMs) in order to separate out the probe signal from the pump before being detected by a 3.5 GHz photodetector and recorded on a digital phosphor oscilloscope with a resolution of 2 ns. As the phase is changed via the pulses, the probe laser sees a change in the reflectivity. The amount of change in the material can be determined by the reflectivity measurement from the probe laser and the temporal dynamics can be gleaned from the resulting graph. In our results we see multiple levels of reflectivity indicating partial change of the GST. After a number of pulses (dictated by the power of each pulse), the reflectivity levels off indicating that the GST is fully changed up to the penetration depth of the laser. From the shape of the graph the cooling times as well as information about the mechanisms of the change can be inferred.

**EP08.04.09** Resistance Drift and Crystallization Processes in the Reset State of GST—Based PCMs **Kazimierz J. Plucinski:** Military University of Technology, Warsaw, Poland.

The amorphous phase in the reset state of GST-based phase-change memory (PCM) cells shows a resistance increase in time according to power law $[1]$ with an exponent dependent on the size of the programmable region. This large increase in resistivity with time (resistance drift) during the ageing of the amorphous phase has up till now limited the multi-level storage capability, i.e. hindered the development of ultrahigh multi-level storage devices. In explanations of the phenomenon of resistivity increase in the reset state of these PCMs published to date, a significant role has been attributed to the creation and growing of subcritical crystalline nuclei inside the amorphous area. The results of analysis of the kinetics of the increase of the population and evolution of subcritical nuclei on the phenomenon of resistivity increase of the amorphous phase in reset state of PCMs are presented here. They are based on previously published research results for compound in the GeTe-Sb$_2$Te$_5$ tie line (e.g. $[2,3]$)


**EP08.04.10** Wide Bandgap Phase Change Chalcogenide Tuned Visible Photonicies **Weiling Dong**, $^1$ Hailong Liu, $^1$ Jitendra Behena, $^1$ Li Lu, $^1$ Ray Ng, $^1$ Kandamathane Sreekanth, $^1$ Xilin Zhou, $^1$ Joel Yang$^1$,$^2$ and Robert Simpson$^1$; $^1$Singapore University of Technology and Design, Singapore, Singapore; $^2$Institute of Materials Research and Engineering, A-STAR, Singapore, Singapore; $^3$Division of Physics and Applied Physics School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Controlling light-matter interactions enables a wide range of applications from optical sensing to imaging and communications. However, for a given nanostructure, the optical response from the light-matter interaction is usually fixed after the device is fabricated. The optical response can be modulated by changing the nanostructure mechanically or by using materials with controllable refractive index. Phase-change materials exhibit a huge property contrast between their structural phases. And the phase transition can be typically invoked in nanoseconds. So far, the most commonly used phase change material for tunable photonicics research is GeSb$_2$Te$_5$. However, GeSb$_2$Te$_5$ is that its absorption coefficient in the visible spectrum is very high, which whilst the change in the real component of the refractive index in the visible spectrum is relatively small. This limits the usefulness of GeSb$_2$Te$_5$ in the visible spectrum. In contrast, SnS$_2$S$_3$, a chalcogenide that has not been studied widely, is a good alternative for visible photonic devices due to its fast switching speed, large optical band gap and large refractive index change. We have shown that by using SnS$_2$S$_3$ in a simple optical resonator, the resonant frequency can be easily tuned by inducing a phase transition in SnS$_2$S$_3$ $[1]$. This phase transition is induced by optical or electrical heating. By changing the thickness and structural state of SnS$_2$S$_3$, the resonant wavelength of the structure can be tuned to cover the whole visible spectrum. Indeed, the maximum resonance shift was 110 nm $[1]$. Note that this simple structure is easily manufactured by industrially scalable techniques. We conclude that SnS$_2$S$_3$-based tunable photonicics is promising for a broad range of applications, such as reconfigurable waveguide systems, spectrometer, and display technologies.

Acknowledgements
This research was performed under the auspices of the SUTD-MIT International Design Center (IDC). The research project was funded by the Samsung GRO, the A*STAR Singapore-China joint research program Grant No. 1402000946, and the SUTD Digital Manufacturing and Design Centre (DManD) Grant No. RGDM 1530302. The authors are grateful for fruitful discussions with Seokho Yun.

SESSION EP08.05: Properties and Applications of Vanadium Oxide
Session Chair: Kotaro Makino
Wednesday Morning, April 24, 2019
PCC North, 200 Level, Room 222 B

8:30 AM EP08.05.01
Fast Periodic Spiking in VO₂ Driven by a Carbon Nanotube Heater
Stephanie Bobaichuk², Suhas Kumar¹, Gregory Pitner², Connor McClellan², Jaewoo Jeong³, Mahesh Samant¹, Stuart S. Parkin¹, H.S. Philip Wong⁴, R. Stanley Williams⁴ and Eric Pop⁵; HP Labs, Palo Alto, California, United States; ²Stanford University, Stanford, California, United States; ³IBM Almaden Research Center, San Jose, California, United States.

The emergence of data-driven computing has prompted a search for systems based on new computational elements. One novel paradigm is the use of spikes, or neuron-like action potentials, to communicate and compute. However, implementing such a neuromorphic system in physical hardware requires compact devices that can produce controllable, low-energy, and fast spiking.

One approach is to exploit instabilities in the transient dynamics of VO₂, which produce periodic spiking when used in a relaxation oscillator, corresponding to periodic heating and cooling across its Mott-metal-insulator transition. Speeding up these devices requires aggressive shrinking to minimize both the electrical and thermal time constants of these oscillations. To effectively scale such VO₂ devices to sub-10 nm widths, in previous work we used metallic carbon nanotubes (CNTs) with ~1 nm diameter as nanoscale heaters in physical contact with an electrically parallel thin film of VO₂ [1].

In this work we demonstrate that a single CNT-VO₂ device forms a Pearson-Anson relaxation oscillator when driven by a DC source, generating neuron-like periodic spiking. The highly localized Joule heating of the CNT acts to trigger and confine the insulator-metal transition in the VO₂ to nanoscale dimensions, greatly reducing the effective thermal mass of the device. This reduction of thermal time constant allows the device to oscillate very rapidly across its Mott transition. Compared to a VO₂-only device, the CNT-VO₂ devices showed a reduction in quasi-static switching voltage accompanied by (a) an increase in the spiking frequency by over 3 orders of magnitude, (b) a decrease in the spike’s transient duration by 3-4 orders of magnitude, and (c) a decrease in pulse energy by 2 orders of magnitude. We also constructed a compact model that could quantitatively reproduce these observations, providing insights into the thermal oscillation effects induced by the CNT.

We further characterized the tunability and scalability of our CNT-VO₂ devices. We found that the spiking frequency of a single device can be tuned by nearly an order of magnitude by adjusting the DC bias conditions. Our results also showed that the spike width and energy decrease with length, with our shortest 300 nm devices showing sub-20 ns spike widths.

In summary, we demonstrated that the addition of a CNT nanoscale heater results in a significant improvement in the dynamical behavior of VO₂-based oscillators. This provides an accessible path to scaling electronic devices by thermally engineering and localizing the dynamics of an otherwise bulk transition mechanism.


8:45 AM EP08.05.02
Thermal Regulation of Space-Craft Using Engineered Vanadium Dioxide Films in Multilayer Optical Coatings
David Woolf, Colin Hesselt, Albert J. Wright and Joel Hensley; Physical Sciences, Inc., Andover, Massachusetts, United States.

Reducing the phase transition temperature of vanadium dioxide (VO₂) to near-room temperature is necessary many thermochromic applications including space radiators. In this work, we demonstrate fabrication of thin films of VO₂ doped with fluorine and tungsten via an aqueous sol-gel method. These films are incorporated into multilayer dielectric stacks that optimize the optical properties of two decades of the electromagnetic spectrum (0.4 - 40 microns) to maintain high solar reflectivity and modulate their emissivity in response to variable heat loads. By doping the films, the phase transition temperature of VO₂ can be reduced from 68 C to less than 30 C, making this technology compatible with both manned and unmanned spacecraft.

9:00 AM EP08.05.03
Boron Doped VO₂ Devices Demonstrating Cycling Dependent Hysteresis
Heidi Clarke¹, Diane G. Sellers¹, Erick Braham¹, Ruben Villarreal¹, Timothy Brown¹, Raymundo Araújo¹, Sampark Banerjee¹ and Patrick J. Shambaeger¹; ¹Chemistry, Texas A&M University, College Station, Texas, United States; ²Materials Science & Engineering, Texas A&M University, College Station, Texas, United States.

Previous investigations on doping of VO₂ to enable tuning of transformation temperature, hysteresis width, and magnitude of the metal-insulator transition (MIT) in VO₂ have primarily focused on substitutional dopants. In a novel post-synthetic diffusive annealing technique, Boron has been introduced as an interstitial dopant which both depresses the phase transition temperature (10 °C/at % B) and introduces an increase of the heating transition temperature as a function of time and temperature below the transition temperature i.e. a thermal history dependence of hysteresis width. Here, the origins of this unique kinetic hysteresis are proposed to stem from B dopant relaxation within the host lattice following the crystallographic phase transition (low-temperature M1 to high-temperature R phase) and will be discussed in the context of structural characterization (near edge x-ray absorption) and density functional theory calculations. Furthermore, in order to probe the effects of B-doping on the resistivity of VO₂, two-terminal devices were photo-lithographically fabricated from single crystal B-doped VO₂ particles with a range of Boron concentrations. Electrical characterization demonstrated that introduction of Boron lowers the resistivity of the low-temperature M1 phase thereby reducing the magnitude of the change in resistivity across the MIT, while introducing a unique kinetic dependence of resistivity. Finally, current pulses will be used to electrically trigger the phase transition to demonstrate viable device behavior. As well as presenting a novel system in which to explore the effect of interstitial dopants on kinetic hysteresis, B-doped VO₂ devices demonstrating varied, kinetically accessible resistance states could be of use in neuromorphic computing applications.

9:15 AM EP08.05.04
Unique Properties of Isostructural VO₂ Thin-Film Heterostructures
Adele Moatti; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Control over the concurrent occurrence of structural (monoclinic to tetragonal) and electrical (insulator to the conductor) transitions presents a formidable challenge for VO₂-based thin film devices. Speed, lifetime and reliability of these devices can be significantly improved by utilizing solely electrical transition while eliminating structural transition. We design a novel strain-stabilized isostructural VO₂ epitaxial thin-film system where the electrical transition occurs at ~77 °C without any observable structural transition. A thin-film heterostructures with a completely relaxed NiO buffer layer has been synthesized allowing a complete control over strains in VO₂ films. We discover that these isostructural thin film devices demonstrating varied, kinetically accessible resistance states could be of use in neuromorphic computing applications.

Acknowledgements
This research was performed under the auspices of the SUTD-MIT International Design Center (IDC). The research project was funded by the Samsung GRO, the A*STAR Singapore-China joint research program Grant No. 1402000946, and the SUTD Digital Manufacturing and Design Centre (DManD) Grant No. RGDM 1530302. The authors are grateful for fruitful discussions with Seokho Yun.
It is observed that the programming current in a memristor is decreased by using 2D materials that emulate the synaptic properties is a crucial building block for brain-inspired computational systems. In today’s data-centric world, where some of the most useful computing tasks are to extract meaningful information from massive amount of unstructured data, neuromorphic computing can provide low-energy high throughput computing. The challenge in data-centric computing with the conventional computing architecture lies in the energy and latency bottleneck of off-chip memory access (i.e. “memory wall”) which do not scale down with the scaling of the technology node. Deep neural network (DNN) is a class of artificial neural networks (ANNs) that benefits from both the availability of big data (large amount of multi-media data for model training) and the continual performance improvement in analog devices in the past decade. However, the memory hierarchy of today’s computing architectures is not specifically designed to leverage the predictive dataflow and potential data reuse of DNN processing, resulting in longer latency and insufficient energy-efficiency for memory access. To reduce these expensive memory access, hardware accelerators for DNNs are designed to employ more fine-grained local memory hierarchy and more specialized dataflow design, which improves the energy efficiency and throughput while maintaining DNN’s inference accuracy. However, the “memory bottleneck” in modern DNNs may not be fully addressed by the acceleration architectures alone. Emerging memory technologies have the potential to play an important and unique role. As these technologies can potentially offer up to tera-bytes of on-chip data storage with a wide range of energy-delay optimization opportunities, they may complement SRAM and DRAM for more efficient DNN inference acceleration. A possible application of the emerging non-volatile memory (NVM) devices is to serve as in-memory computing element where multi-level resistance response of an NVM can store the analog synaptic weights of a DNN on-chip. In another in-memory computing scheme, a crossbar array of non-volatile memory devices can perform the multiply-and-accumulate (MAC) operation at a lower energy cost when the input vector is encoded as an analog voltage and the weight matrix is encoded as analog resistance (conductance) values stored in the memory devices. The ability of the NVMs like RRAM, PCM, CBAM to change its resistance values gradually as a function of the applied voltage pulse across its electrode is the key to performing analog in-memory MAC operation. This paper provides an overview of the current state-of-the-art non-volatile memory devices used for neuromorphic hardwares in applications ranging from biology based learning models to conventional machine learning algorithms solved using neural networks. Furthermore, a more focused overview of the device-level trade-offs required for hardware acceleration of neural network architectures using analog in-memory MAC operation is presented. In general, larger conductance range, more intermediate states, and higher resistance are desirable for both inference and training. For inference, an ideal device should also have linear I-V relationship and long retention time. For training, symmetric and linear pulse response, small device-to-device and cycle-to-cycle variation, and good endurance are crucial. Our review reveals that controlling the oxygen ion movement during pulse switching in RRAM can be a promising way to achieve the aforementioned performance goals. Placing an oxygen ion barrier to make a bilayer RRAM and confinement of the generated heat during switching have shown significant improvement in analog switching. Better thermal management in RRAM can also provide filament stability that could improve reliability like retention and endurance. If the ideal device can be achieved, the MAC array using NVMs can provide ultra-low energy, high throughput computing without compromising bit precision that is currently missing in the neural network accelerator landscape.
Ferroelectrics as phase-transition materials have promising applications in both logic and memory technologies beyond CMOS. Neuromorphic architectures, such as neural networks and artificial brains [1][2], require synergy among neurons and synapses to achieve cognition and classification functionalities. In spite of the fact that traditional CMOS technologies provide some topology to achieve these functionalities, emerging devices, such as ferroelectrics field-effect-transistors (FEFETs), offer significant benefits in terms of power, performance, and area as physical platform for implementing neural networks due to their unique properties—hysteresis, non-volatility, multi-state, and etc. In the past a few years, FEFETs have demonstrated great potential in implementing artificial synaptic devices [3]-[5]; however, the demonstration of artificial neurons built on ferroelectric devices is still pending. In this talk, we will present experimental demonstration of ferroelectric spiking neuron based on a compact IT-1FFETT structure and projected performance of spiking neural network based on ferroelectric neurons for unsupervised clustering on MNIST dataset [6]. Ferroelectric spiking neurons utilize abrupt hysteric transition feature of ferroelectrics such that there are unstable states in the current-voltage characteristics of FEFETs [7]. FEFET hysteresis can be dynamically tuned by bias conditions which allows for inhibition functionality. Artificial neurons based on metal-semiconductor-metal transition (MIT) devices [8], suffer from a fundamental shortcoming—all these neurons are excitatory. In contrast, ferroelectric spiking neurons have built-in excitatory and inhibitory input connections, which are essential to enable high accuracy in unsupervised learning, increases sparsity in spiking, and efficient implementation of synaptic weights.

In summary, spiking neurons based on FEFETs provide compact and efficient implementation of artificial neurons and have great potential in developing spiking neural networks and other neuromorphic applications.

Reference:
individual vias connecting the resulting network to electrode pads were written and deposited. Network quantifying simulations revealed a small-world coefficient of 2.89, shortest path length of 3.61 and clustering coefficient of 0.057. When electroformed, this system exhibited switching between LRS and HRS at ±7 V. To investigate the role of electrode-membrant interfaces, copper tungsten films were deposited on copper substrates using chemical solution deposition. After patterning top tungsten electrodes and electroforming, IV measurements revealed memristive behavior and exhibited switching between LRS and HRS at ±0.7 V. In this presentation, the fabrication process and the memristive characteristics (endurance, resistance retention, pulse measurements, etc.) of the above listed systems will be discussed in detail.

11:45 AM EP08.06/EP09.05.07

Inspired by neural computing, the pursuit of ultralow power neuromorphic architectures with highly distributed memory and parallel processing capability has recently gained more traction. However, emulation of biological signal processing via artificial neuromorphic architectures does not exploit the immense interplay between local activities and global neauron modulations observed in biological neural networks, and hence are unable to mimic complex biologically plausible adaptive functions like heterosynaptic plasticity and homeostasis. Here, we demonstrate emulation of complex neuronal behaviours like heterosynaptic plasticity, homeostasis, association, correlation and coincidence in a single neuristor via a novel dual-gated architecture. This multiple gating approach allows one gate to capture the effect of local activity correlations and the second gate to represent global neuron modulations, allowing additional modulations which augment their plasticity and enabling higher order temporal correlations at a unitary level. Moreover, the dual-gate operation extends the available dynamic range of synaptic conductance while maintaining symmetry in the weight-update operation, expanding the number of accessible memory states. Finally, operating neuristors in the sub-threshold regime enables synaptic weight changes with high gain, while maintaining ultralow power consumption of the order of femto-Joules.

SESSION EP08.07: Threshold Switching Behavior and Selector Device
Session Chair: Marie-Claire Cyrille
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 222 B

1:30 PM EP08.07.00
A New Approach to Accessing the Semiconductor-to-Metal Transition in Two-Dimensional Crystals Using Ionomers Susan Fullerton, Ke Xu, Aaron Woeppe1, Jierui Liang, Eli Bostian, Hangjun Ding and Eric Beckman; Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Many approaches to induce the semiconductor-to-metal phase transition in two-dimensional (2D) crystals via strain involve global strain of the entire substrate as opposed to local strain of individual devices. In this work, we present a new approach to induce the transition where individual devices are addressed via field-effect modulation of an ionomer (i.e., single-ion conductor). Specifically, strain is induced in each device using a voltage applied to the top gate of an electric-double layer (EDL)-gated, field-effect transistor (FET). The mechanism to induce strain is the same mechanism responsible for actuation in ionic polymer metal composites (IPMC’s), which mimic the behavior of muscle. The active layer in an IPMC is a single-ion conductor, which deforms under applied voltage due an electrostatic imbalance created by the formation of an EDL on one polymer/electrode interface but not the other. The imbalance occurs because only cations, and not anions, are free to diffuse in the electrolyte. Modeling indicates cation densities up to 5 x 10^4 ions/cm^2 at the ionomer/electrode interface under 2V applied gate bias, which is theoretically predicted to induce several percent strain on the 2D crystal—enough to induce the phase transition. Experimentally, a custom-synthesized ionomer is used to electrostatically gate both graphene and MoTe2 FETs. Compared with backgating through SiO2, transfer characteristics on both EDL-gated graphene and MoTe2 FETs reveal a similar enhancement of the n-branch using both the ionomer and a dual-ion conductor (i.e., one with mobile cations and anions). The ionomer decreases the subthreshold swing in the n-branch of the MoTe2 FET from 5000 to 250 mV/dec and increases the current density and on/off ratio by two orders of magnitude. However, as expected, the ionomer quenches the p-branches in both the graphene and the MoTe2 FETs because the anions are immobilized and therefore cannot form an EDL by inducing holes in the channel. This is the first demonstration of an ionomer-gated 2D FET and it lays the groundwork for further simulate a phase change memory device in series with an OTS using our finite element phase change model [6]–[8].

EP08.07.01

Phase change memory is a resistive non-volatile memory technology that stores information in the crystalline (conductive) or amorphous (resistive) phase of a material such as the chalcogenide Ge2Sb2Te5. Phase change memory can be implemented as a crossbar array, allowing for very dense storage, and it is back-end-of-line compatible, allowing for on-chip fabrication to eliminate the von Neumann (off-chip memory access) bottleneck. Crossbar arrays connect many devices in parallel with individual devices read and written by selecting the appropriate word and bit lines. They are susceptible to large leakage currents due to the many parallel devices between non-selected and selected lines, and thus require a current limiting access device in series with every memory cell. Ovonic threshold switches (OTSs) are such devices. OTSs are highly resistive in the off state but switch to a highly conductive on state at some threshold voltage due to a field-dependent conductor mechanism in amorphous chalcogenides. They remain on while a minimum holding current passes through the device, then rapidly switch off. As access devices, OTSs must be designed such that all unselected devices remain off while a selected device passes enough current to read or write a memory cell regardless of the initial state of any memory cell in the array [1]. However, there is still debate on the mechanism(s) behind ovonic switching and thus on how a given design will behave. Recent models that explain ovonic switching include (i) field-based switching due to the filling of trap states near the fermi band in amorphous Ge2Sb2Te5 (a-GST) [2], (ii) field-assisted crystallization, where crystals are stable in phase change materials and unstable in OTSs once the field is removed [3], and (iii) a field-assisted thermal phenomenon in doped a-GST [4]. We model ovonic switching in a-GST as a field-assisted thermal phenomenon by coupling field and temperature dependent conductivity terms [5], simulate switching in COMSOL Multiphysics, and find good agreement with experimental ovionic switching data for a-GST. We further simulate a phase change memory device in series with an OTS using our finite element phase change model [6]–[8].


2:00 PM EP08.07.02
Volatile Threshold Switching and Non-Volatile Bipolar Resistive Switching in Mixed Phased a-VOx Asymmetric Crossbar Devices Shrinu Nirantar, Md. Ataur Rahman, Mohammad Taha, Taimur Ahmed, Matthew Field, Madhu Bhuskaran, Sumeet Walia and Sharath Srinivas; School of Engineering, RMIT University, Melbourne, Victoria, Australia.

Vanadium oxide shows versatile properties which can be triggered using temperature as well as electric bias. Due to this, it has been proven to be a potential material in the field of resistive random access memory both as a memory element and selector. Here, we fabricate asymmetric cross-points devices of amorphous vanadium oxide films to analyse its
resistive switching performance related to different oxide phases as well as phase-change induced insulator-to-metal transition. Devices show a characteristic volatile threshold switching after electroforming at high voltages, whereas lower voltages reveal a forming-free non-volatile bipolar resistive switching behaviour. Volatile switching performance is apolar, stable, reversible, and symmetric for over 10^4 consecutive cycles. While, non-volatile bipolar resistive switching is asymmetric and stable over 200 cycles. Based on the achieved electrical characterisation and compositional analysis, it is suggested that the volatile threshold switching is due to the presence of VO₂ component, while non-volatile switching is due to the presence of V₅O₄ component in the mixed phase amorphous vanadium oxide film. This work highlights the occurrence of bifunctional memory behaviour in amorphous cross-point devices and further provides guidelines to tailor the switching behaviour.

2:15 PM EP08.07.03
Operation and Materials Choice for Chalcogenide Selector Devices
John Robertson; Cambridge University, Cambridge, United Kingdom.

The electronic structure and conduction mechanism in chalcogenide-based Ovonic threshold switches (OTS) used as selectors in cross-point memory arrays is derived from density functional calculations and quasi-Fermi level models. The experimentally most favorable compositions are found to lie in the 4:2 coordinated region of the phase stability maps of IV-VI semiconductors. The switching mechanism in OTS is primarily electronic. It uses a specific electronic structure, with a wide tail of localized states below the conduction band edge. In amorphous GeSe₂-x the valence band top consists of high effective mass Se pt states with few band tails. The conduction band consists of Ge-Se antibonding states with low effective mass, and with a broad tail of localized Ge-Ge antibonding states below this band edge. This leads to the OTS behavior. At high fields the electron quasi-EF moves up through these tail states, lowering the conductivity activation energy, and giving the non-linear switching process. GeSe₂-x is the most favorable OTS material because it has the optimum band gap.

2:30 PM BREAK

SESSION EP08.09: Phase Change Device Characterization
Session Chair: Juuni Tonnaga
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 222 B

3:30 PM *EP08.08.01
Fundamental, Thermal and Energy Limits of Phase-Change Memory
Eric Pop, Christopher Neumann, Sanchit Deshmukh, Isha Datye, Stephanie Bohaichuk and Miguel Munoz Rojo; Electrical Engineering and Materials Science and Engineering, Stanford University, Stanford, California, United States.

The reversible material phase transition in chalcogenide compounds, known as phase-change memory (PCM) has been studied for half a century [1]. More recently, some PCM devices have been approaching the fundamental scaling limits of this technology [2]. This talk will present recent highlights from our research on PCM and related materials [3]. The results span from measurements of thermal and electrical properties of PCM devices and their interfaces, to understanding their fundamental size and energy limitations. For example, we show that the energy-efficiency of PCM programming can be significantly improved by reducing the pulse width (down to few nanoseconds). We use Raman thermometry and scanning thermal microscopy (SThM) to probe the temperature in functioning PCM devices [4,5], and uncover thermal and electrical contact resistance effects. We also introduce PCM devices which rely on emerging two-dimensional (2D) materials like graphene or MoTe₂, either as thermal insulation barriers [6] or as the switching material itself. Finally, we use carbon nanotubes (CNTs) as ultra-narrow electrodes to probe the insulator to metal (ITM) transition of VO₂ at the nanoscale. These results probe the fundamental limitations of PCM technology, as required to guide future energy-efficient designs.


4:00 PM EP08.08.02
Computational Analysis of Complex Amorphization/Crystallization Dynamics in Large Phase Change Memory Devices

Phase change memory devices become practical for non-volatile storage at small dimensions due to reduced power and predictable device operation. In larger scale devices, cells can be locally melted due to filament formation and liquid filaments can be retained in parts of the cell for a long time even if most or all of the cells are initially amorphized during long fall-times. The complex amorphization and crystallization dynamics make these large cells more unpredictable and enable their applications as physically unclonable functions (PUF) [1,2].

Computational analysis of the complex amorphization-crystallization dynamics in phase change memory devices with large geometries is important to understand the evolution of phase distributions and temperature profiles during programming of these devices. In this work, we conduct electrothermal finite element simulations of reset operation on a large GeSb₂Te₅ (GST) cell using the framework we have developed in COMSOL multiphysics [3]-[9] and analyze the complex dynamics of amorphization, nucleation and growth during electrical stress. We input voltage waveforms measured from electrical characterization of on-oxide GST line cells with bottom metal contact pads and SiNₓ capping. A 2D polycrystalline model of the experimentally measured cells (~360 nm wide, ~400 nm long and ~50 nm thick) is constructed in the simulations. Access devices are modeled using the spice models. The simulations capture some of the interplay between changes in the device resistance due to heating and phase changes and current fluctuations.

References:

4:15 PM EP08.08.03
Investigation of Resistance Drift in GeSb₂Te₅ Phase Change Memory Line Cells at Low Temperatures—Contributions of Charge Trapping
ABM Hasan Talukder, Rajan Saeed Khan, Kimberly Nguyen, Madison Nadolny, Nafisa Noor, Faruk Dirisaglik, Adam Cywar, Sadid Muneer, Helena Silva and Ali Gokirmak; Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States; ²Electrical and Electronics Engineering, Eskişehir Osmangazi University, Eskişehir, Turkey.
Phase change memory (PCM) is one of the most promising non-volatile memory technologies that offers low-power, high-speed, and high-density operations. PCM utilizes the large resistivity contrast between amorphous and crystalline phases of chalcogenide materials such as Ge\(_2\)Sb\(_2\)Te\(_5\) (GST). The large resistivity contrast between the phases allows multilevel-cell (MLC) operation, which comes with some challenges including the upward resistance drift observed in PCM cells. A cell programmed to a certain state, if experiences resistance drift, may be incorrectly read some time after programming.

High-speed electrical characterization techniques allow us to monitor resistance drift behavior of the amorphous GST cells for a very short duration [1] and the slow DC measurements can be used to monitor the drift over a long period of time [2]. Our earlier resistance drift measurements were performed in 300 K to 675 K range [1]. In this work, we have amorphized GST line cells at cryogenic temperatures (down to 85 K) and monitored their resistance drift. We observe significant resistance drift of the amorphous GST at low temperatures. The viscosity of the material is expected to be very high to allow any significant structural relaxation at these low temperatures. Furthermore, we observe significant sensitivity to light: cells exposed to light for a period of time show a drop in resistance, and a recovery of the resistance after light is blocked. The time scale for these changes are in the order of seconds to minutes, suggesting that the changes in the resistance are predominantly due to emptying and filling of charge traps, and not due to thermal perturbations on the cells due to exposure to light.

Since we do not expect a rapid change in the number of charge traps via structural relaxation at cryogenic temperatures, our observations point to filling of the existing charge traps (charge trapping) as the main reason for upward resistance drift in phase change memory cells. Based on these results, we predict that it is possible to suppress resistance drift by increased capacitive coupling between the active region of PCM cells and the surrounding electrodes.

References:

4:30 PM EP08.08.04 Evaluating PCM Asymmetry by a Three-Terminal Device Kirill V. Mitrofanov, Yuta Saito, Noriyuki Miya, Paul Fons, Alexander Kolobov and Janji Tominaga; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Interfacial phase-change memory (iPCM) devices based on a Ge-Te/Sb-Te superlattice have lower switching energy than conventional phase-change memory due to optimization of the structure of the chalcogenide layers allowing minimization of the thermal losses associated with the switching process [1]. To date it has been widely believed that the structural changes responsible for switching in iPCM occur at the interfaces of the superlattice structure [2-4]. Recently, however, it has been proposed that resistive switching in iPCM may occur within a very narrow region of the superlattice device structure that has a specific atomic ordering. In the current work, the superlattice volume that is switched in iPCM was minimized by introducing a laterally connected contact to the superlattice film located between the two contacts perpendicular to the superlattice growth direction (van der Waals gaps plane in a superlattice structure). The resultant three-terminal iPCM device allowed the testing of selective regions of the device. This configuration is especially useful for the characterization of asymmetric iPCM devices and bipolar switching performance. The latter is believed to be related to the contact interfaces, which could be identified by the use of the third electrode. Previously, it was shown that iPCM devices based on Ge-Te/Sb-Te superlattices have a different switching thermal dependence than alloy-based phase-change memory [5]. In addition, multi-level and bipolar switching and external magnetic field effects [6] of iPCM devices resistance were found. The newly proposed device structure will allow for detailed characterization of these effects as well as the partial volume switching of iPCM.

In conclusion, the dependence of iPCM switching on the distribution of the applied switching electric field within the volume of Ge-Te/Sb-Te superlattices was studied with the use of a three-terminal device architecture. The effects of bipolar switching, high temperature operation and external magnetic field were assessed.

This work was supported by JST-CREST (JPMJCR14F1). A part of this study was supported by NIMS Nanofabrication Platform in Nanotechnology Platform Project sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.


4:45 PM EP08.08.05 Multi-Contact Phase Change Toggle Multiplexer Raihan Sayeed Khan, Nadim H. Kar’an, Jake Scoggin, Zachary Woods, Helena Silva and Ali Gokirmak; University of Connecticut, Storrs, Connecticut, United States.

Phase change memory (PCM) is a non-volatile memory technology which utilizes resistance contrast of amorphous and crystalline phases of phase change materials such as Ge\(_2\)Sb\(_2\)Te\(_5\) (GST). PCM cells are two-contact devices which offer fast read/write speed, high density, large endurance, and possibility of monolithic integration with CMOS at the back-end-of-the-line. There has been a growing interest in integration of PCM devices for computation in memory and neuromorphic computing. It is possible to implement logic functions, multiplexing and data routing using phase change elements with multiple contacts [1], [2]. The logic functionality is achieved using two physical mechanisms that can be implemented at nanoscale: (i) isolation of some of the contacts from the others using local amorphization between other contact pairs, (ii) thermal cross-talk between the regions that are heated to be melted and the previously amorphized regions. The first allows for isolation of some of the input and the output terminals, and the second allows for toggle operations through crystallization of some regions while others are being amorphized. 6-contact phase-change devices can be implemented as toggle multiplexers or flip-flops when interfaced with 5 CMOS transistors, using ~50% CMOS footprint compared to the conventional CMOS alternatives with the added advantage of non-volatility. This approach can enable monolithic integration of 100s of GB of PCM atop CPUs for computer-on-chip applications.

We have performed a 2D computational analysis of six-contact phase change logic devices using our finite element framework that can simultaneously capture amorphization-crystallization dynamics including nucleation, growth, and grain boundary melting and electro-thermal phenomena in COMSOL Multiphysics [3]–[5]. Our analysis includes structural changes responsible for switching in iPCM occur at the interfaces of the superlattice structure [2-4]. Recently, however, it has been proposed that resistive switching in iPCM may occur within a very narrow region of the superlattice device structure that has a specific atomic ordering. In the current work, the superlattice volume that is switched in iPCM was minimized by introducing a laterally connected contact to the superlattice film located between the two contacts perpendicular to the superlattice growth direction (van der Waals gaps plane in a superlattice structure). The resultant three-terminal iPCM device allowed the testing of selective regions of the device. This configuration is especially useful for the characterization of asymmetric iPCM devices and bipolar switching performance. The latter is believed to be related to the contact interfaces, which could be identified by the use of the third electrode. Previously, it was shown that iPCM devices based on Ge-Te/Sb-Te superlattices have a different switching thermal dependence than alloy-based phase-change memory [5]. In addition, multi-level and bipolar switching and external magnetic field effects [6] of iPCM devices resistance were found. The newly proposed device structure will allow for detailed characterization of these effects as well as the partial volume switching of iPCM.

In conclusion, the dependence of iPCM switching on the distribution of the applied switching electric field within the volume of Ge-Te/Sb-Te superlattices was studied with the use of a three-terminal device architecture. The effects of bipolar switching, high temperature operation and external magnetic field were assessed.

This work was supported by JST-CREST (JPMJCR14F1). A part of this study was supported by NIMS Nanofabrication Platform in Nanotechnology Platform Project sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References:
Phase-change memory (PCM) is an industrial concerned technology that can be used both for traditional computer architecture and other new emerging architectures [1], such as in-memory computation. Generally, the transitions between order and disorder phases are employed to record data. However, one of the drawbacks of PCM is the relatively high power consumption. Therefore, controlling the transition without going through the amorphous phase in these materials is one of possible methods to reduce switching energy. In this talk, we will introduce two cases recently explored with DFT calculations for order-order transition for PCM materials. The first case is the stacking-fault motion induced Insulator-metal transition in GeTe:Sn:Te superlattices [2]. This transition may provide a significant change of carrier concentration and indicate a low energy-consumption process with a low energy barrier of atom motion for PCM. Secondly, we have developed multi-phase-field model for the crystallization of GST which takes into account three phases: the amorphous state, stoichiometric GST and a Ge-rich crystalline phase. We use a pseudo-binary approximation of the phase diagram and couple the phase fields to a single concentration field. The kinetic parameters of the model are determined from data on stoichiometric GST available in the literature [4]. As a first application, we study the isothermal crystallization of a homogeneous Ge-enriched amorphous GST film. The critical nuclei of the Ge-rich crystalline phase are always computed, and the results are compared to classical nucleation theory. Growth of supercritical nuclei is then simulated, and the results are compared to recent experimental data [5].


9:30 AM EP08.09.02
Multi-Phase-Field Modelling of Microstructure Formation During the Non-Congruent Crystallization of an Amorphous Alloy of Germanium, Antimony and Tellurium Raphaël Marie1, 2, Olga Cuetel, Serge Blonkowski, Thomas Philippe and Mathis Plapp, PMC Ecole Polytechnique/CNRS, Palaiseau, France; STMicroelectronics, Grenoble, France; CEA LETI, Grenoble, France.

Phase change materials (PCM) can exist in two different states, namely, as amorphous and crystalline solids, which can have markedly different physical properties. This is the basis for the usage of PCM for data storage applications. The ternary alloy of germanium, antimony and tellurium (GST) has been intensely studied, because at the stoichiometric composition Ge5Sb2Te12, the amorphous phase can crystallize congruently (without changing in composition) and rapidly. This makes it a material of choice for random access memory devices (pc-RAM). However, the amorphous phase spontaneously crystallizes at relatively low temperature (160 °C). For automotive applications, this temperature has to be increased, for example by enriching the stoichiometric GST with germanium [1]. However, then the crystallization is accompanied by a composition change: upon crystallization, the additional Ge segregates into the amorphous phase, which can lead to the nucleation and growth of a new crystalline phase which is rich in Ge. For the development of new materials for automotive applications devices, it is important to better understand this complex microstructure formation process.

Phase-field models are continuum models based on nonequilibrium thermodynamics [2,3]. Interfaces and surfaces are implicitly described by one or several scalar fields that often can be identified with order parameters. Their time evolution is naturally coupled to the transport of chemical components by diffusion. We have developed a grand-canonical multi-phase-field model for the crystallization of GST which takes into account three phases: the amorphous state, stoichiometric GST and a Ge-rich crystalline phase. We use a pseudo-binary approximation of the phase diagram and couple the phase fields to a single concentration field. The kinetic parameters of the model are determined from data on stoichiometric GST available in the literature [4]. As a first application, we study the isothermal crystallization of a homogeneous Ge-enriched amorphous GST film. The critical nuclei of the Ge-rich crystalline phase are always computed, and the results are compared to classical nucleation theory. Growth of supercritical nuclei is then simulated, and the results are compared to recent experimental data [5].


9:45 AM EP08.09.03
Ultrafast Photo-Induced Phase Transition in 2D MoTe2: Bo Peng1, 2, Hao Zhang1 and Heyuan Zhu1; 1Fudan University, Shanghai, China; 2University of Cambridge, Cambridge, United Kingdom.

Using first-principles calculations, we confirm that purely electronic excitation plays a dominant role in laser-induced phase transition of MoTe2. This unique effect is induced by ultra-rapid bond dissociation. Under different wavelength laser excitation, the potential energy surface for lattice vibrational modes can be modified precisely to generate the intermediate phase along the phase transition pathway, enabling controllable phase transformation. The excited carrier concentrations at different excitation energies are estimated. Moreover, we find that the laser-generated local heat cannot account for thermally-induced phase change. The photo-induced phase transition can occur within hundreds of femtoseconds before the excited electrons transfer their energy to the lattice. Taking advantage of optically-induced electronic excitation, a rapid and controllable phase transformation with sub-micron precision can be realized in monolayer MoTe2, opening a new door for precise control of selective phase transition by tuning laser wavelength.

10:00 AM BREAK

10:30 AM *EP08.09.04
A Machine-Learned Interatomic Potential for the Elemental Phase Change Material Sb Daniele Dragone1, Joerg Behler2 and Marco Bernasconi1; 1University of Milano-Bicocca, Milano, Italy; 2Institute for Physical Chemistry and Theoretical Chemistry, University of Goettingen, Goettingen, Germany.

Elemental antimony has been recently shown to be a suitable material for electronic phase change memories (PCM) when confined in ultrathin films [1]. Despite the extreme proneness to crystallization in the bulk, amorphous Sb has been demonstrated to be stable at 300 K for sufficiently long time to be used in PCM when it is grown in films as thin as 3 nm confined by capping layers [1]. The reasons behind the amorphization of the phosphorus phase under these conditions are, however, unclear. Atomistic simulations can provide insights onto the several effects that might concur to stabilize the amorphous phase in confined geometry. To this end, we have generated an interatomic potential for antimony by using a machine learning approach, namely by fitting a large database of ab-initio energies by means of the neural network scheme introduced by Behler and Parrinello [2]. The same method was used previously to generate an interatomic potential for the phase change compound GeTe [3]. The potential has been validated by computing the structural properties of the crystalline, amorphous and liquid phases of bulk antimony. Then molecular dynamics simulations based on the neural network potential have been performed to investigate the crystallization kinetics of Sb in confined geometries. Possible effects on the crystallization kinetics induced by the presence of the capping layer in ultrathin films will be discussed.


11:00 AM EP08.09.05
Effects of Si Doping on the Electronic Structure and Electrical Conductivity of Ge5Sb2Te12 Crystals—First-Principles Study Rajarshi Sinha Roy, Magali Benoit and Lionel Calmels; CEMES, CNRS, Université de Toulouse, Toulouse, France.

The transport properties of Ge-Sb-Te (GST) ternary phase-change materials can be tuned by controlling their atomic structure and the concentration of charge carriers. Doping with atoms of different chemical species is a major method to reach this aim in GST crystals. The effects of doping on the transport properties of GST are challenging to study
experimentally, since the crystalline phase of doped GST samples generally possesses a complicated microstructure, consisting of grains with different compositions. They are also challenging to investigate by first-principles methods based on the calculation of Kohn-Sham wave functions, as huge supercells are needed to describe the unavoidable chemical disorder among Ge, Sb, dopant atoms, and vacancies.

In this work, we perform first-principles calculations of the electronic structure and electrical conductivity of Si-doped GST ec-crystals, using the spin polarized relativistic Korringa-Kohn-Rostoker (KKR) method based on the multiple-scattering theory [1,2]. The doped GST crystals have been described with a rock-salt unit cell, in which the chemical disorder is taken into account through the coherent potential approximation (CPA). The accuracy of the results is verified by comparing, for several Si contents, the density of electronic states (DOS) calculated with this method and with a method that uses Kohn-Sham wave functions in big supercells. The calculated Bloch spectral function (BSF) shows the dispersion of the electron states and its modification with doping. We show the Si-doping dependence of the electrical conductivity, and discuss it in terms of the concentration of charge carriers and of the modification of their scattering by the atomic disorder induced by doping. These results can be used to model samples, the microstructure of which consists of grains with different concentrations of Si atoms, each grain being described by a conductivity that depends on its composition.

References:

11:15 AM EP08.09.06
The Role of Electric Fields in the Structural Rearrangements of iPCM Building Blocks

Paul Fons1, Alexander Kolobov1, Yuta Saito2, Kotaro Makino1 and Junji Tominaiga3
1 Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 2Spring8, Japan Synchrotron Radiation Institute (JASRI), Hyogo, Japan.

One of the more active research areas in phase-change memory is the concept of van der Waals (vdW)-bonded GeTe/Sb2Te3 superlattices (SL) also known as interfacial phase-change memory (iPCM). Devices based upon GeTe/Sb2Te3 SL structures have demonstrated both lower energy consumption as well as order of magnitude faster switching speeds. Unlike conventional Ge-Sb-Te alloy-based devices in which the SET and RESET states correspond to the crystalline and amorphous phases, the SET and RESET states in SL change memory (iPCM). Devices based upon GeTe/Sb2Te3 SL structures have demonstrated both lower energy consumption as well as order of magnitude faster switching speeds.

As electrical device components are scaled down to atomic sizes, management of waste heat becomes a major issue in device performance. Minimizing energy consumption of electrical components and waste heat generation are critical issues in the operation of electronic devices. This has spurred interest in alternative cooling mechanisms, such as those provided by electrocaloric, magnetocaloric, elastocaloric, and thermoellectric materials, for mitigating issues associated with waste heat generation. In this work, we provide theoretical predictions for an alternative cooling mechanism, accomplished by utilizing electrostatic gating to induce structural phase transitions in monolayer materials. We refer to this mechanism as the electrostaticaloric effect in reference to the mechanism of electrostatic doping that drives the structural phase transformation and entropy change in the material. Recent predictions and experimental observation that electrostatic gating can induce structural phase transitions in monolayer materials opens the possibility for new application areas. Here, we explore the potential for electrostatically-induced structural phase transformations in monolayer MoTe2 to be used in a Carnot refrigeration cycle. We predict that a temperature change of 10–15 K may be possible in devices that utilize monolayer MoTe2 as the active phase change material. This mechanism may prove useful for future electronic devices which require cooling at the component level, and for which small monolayer devices are necessary.

11:30 AM EP08.09.07
Refrigeration in Two-Dimensions—Electrostaticaloric Effect in Monolayer Materials

Daniel A. Rehn1,2, Yao Li1 and Evan Reed1, 1Stanford University, Stanford, California, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

As electrical device components are scaled down to atomic sizes, management of waste heat becomes a major issue in device performance. Minimizing energy consumption of electrical components and waste heat generation are critical issues in the operation of electronic devices. This has spurred interest in alternative cooling mechanisms, such as those provided by electrocaloric, magnetocaloric, elastocaloric, and thermoellectric materials, for mitigating issues associated with waste heat generation. In this work, we provide theoretical predictions for an alternative cooling mechanism, accomplished by utilizing electrostatic gating to induce structural phase transitions in monolayer materials. We refer to this mechanism as the electrostaticaloric effect in reference to the mechanism of electrostatic doping that drives the structural phase transformation and entropy change in the material. Recent predictions and experimental observation that electrostatic gating can induce structural phase transitions in monolayer materials opens the possibility for new application areas. Here, we explore the potential for electrostatically-induced structural phase transformations in monolayer MoTe2 to be used in a Carnot refrigeration cycle. We predict that a temperature change of 10–15 K may be possible in devices that utilize monolayer MoTe2 as the active phase change material. This mechanism may prove useful for future electronic devices which require cooling at the component level, and for which small monolayer devices are necessary.

SESSION EP08.10: Crystal Growth and Structure
Session Chair: Daniele Dragoni and Xiaobin Li
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 222 B

1:30 PM EP08.10.01
Synthesis and Characterization of TaS3-Based Superlattices for Applications in Electrically-Driven Quantum Phase Transitions

Saez Baurx, Demissie M. Roberts, John D. Perkins and Andriy Zakutayev; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

Typical phase-change materials used in microelectronics rely either on amorphous-crystalline transitions or on redox reactions. Each of these mechanisms rely on slow and energy-intensive processes, such as heating and quenching or solid-state ion diffusion. Another approach without these drawbacks is to use materials with quantum phase transitions, but these are generally activated and maintained thermally rather than electrically. However, some reports exist of electrically-activated charge-density wave (CDW) transitions, which are similar to a Peierls distortion and sometimes observed in low-dimensional materials.

Inspired by work in selenide-based superlattices, where charge exchange between layers can modulate an emergent CDW transition, our group is working on synthesis and characterization of superlattices based on a well-known CDW material, TaS3. Using the novel approach of depositing thin modulated layers of Ta and Sn that are combinatorially sputtered from metallic targets in the presence of sulfur plasma, we build libraries of such superlattices from the “bottom-up.” This is new because sulfide based superlattices have not been previously made using this approach. The deposition process is monitored using quartz crystal microbalances, which provide real-time in-situ feedback on the growth conditions.

Our x-ray reflectivity results show that we can form ultrathin smooth films with control of the integer number of 2D monolayers in the repeating structure. We have also demonstrated that by altering deposition conditions we can vary sulfur content and adjust composition to promote formation of either SnS5 or SnS3 layers, according to RBS measurements. Similar to selenium-based superlattices, changing layer thicknesses is expected to affect the electrical transport properties, since this changes the degree of charge transfer between the layers. Overall, the initial results from this work suggest that a similarly superlattice-modulated CDW phase transition may be observed in TaS3-based superlattice materials.
The crystallization process of phase change materials has been largely investigated in literature in a wide range of temperature and for many compositions. On the contrary, there is a lack of information on the mechanisms governing the amorphization, since it can be obtained only by driven conditions, largely far from equilibrium, usually implying melting and quenching. Understanding which are the accessible local atomic configurations towards amorphization and how atoms move through a crystalline environment, even highly defective, hence, seems desirable. With this aim we have investigated the damaging process of crystalline GeSbTe alloys up to amorphization, by using ion irradiation. Irradiation with light ions (Ar$^+$) has been adopted to produce diluted cascades, which allows very low amount of disorder to be introduced and to follow the structural evolution towards complete amorphization.

In situ reflective measurements and ex-situ resistance and Raman spectroscopy analysis have been employed to study the disordering process and its impact on the electrical properties and on the chemical bonds. Different compositions are compared: Ge$_7$Sb$_5$Te$_9$, Ge$_9$Sb$_8$Te$_7$ and Ge$_8$Te$_5$. The effect of disordering is studied at low temperature (77K), at which the atomic mobility and disorder recovery is hindered, and at room temperature. For all the studied compositions large differences are observed upon irradiation at low or room temperature, indicating that there is a large effect of dynamic annealing. Several phase transitions are observed before amorphization. In all the cases, the first is the metal to insulator transition. However, the mechanism driving such a transition is different changing from the ternary compositions to the binary GeTe. Indeed, in the case of crystalline GeSbTe alloys (with Ge < 30%) the disordering process is dominated by the presence of the stoichiometric vacancies. The van der Waals like gaps present in the stable hexagonal crystalline structure act as preferential sink for the diffusion of the displaced atoms, and are therefore effective in stabilizing the disordered material. The filling of the gaps tunes the electronic and structural properties, driving the metal-insulator transition and the successive conversion into the metastable rocksalt structure and then in the amorphous.

In the case of GeTe there are no structural vacancy layers. The metal-insulator transition, observed at very low fluences, occurs in a mainly crystalline material with low resistivity value (~0.5 mOhm cm) and, according to Raman spectroscopy investigation, seems to be induced by Te vacancy, characterized by an energy level into the gap. As the irradiation fluence increases the displaced atoms form distorted octahedral bonds that, being energetically unfavourable, tend to disappear, going back to a more stable configuration. Such a process seems to be facilitated by the high atomic mobility that, according to crystal growth rate data available in literature, at room temperature is expected to be larger in GeTe than in GeSbTe alloys. As a consequence, GeTe exhibits unique marked self-healing properties and the irradiation fluence required for complete amorphization is one order of magnitude higher than that of GeSbTe alloys.

The role of the interfaces on the amorphization process has been also investigated and we found that by properly choosing the substrate and the capping layer it is possible to reduce or enhance the stability of the amorphized state. On the other hand we concluded that the interfacial high-atomic mobility is the key parameter to the amorphization.

Our results indicate the possibility to tune the structural and electrical properties by interface and/or by defects engineering. Such an approach could help to avoid the employment of complex compositions, usually needed to finely tune the material properties, but which, on the other hand, can produce reliability problems, related to unwanted deviations from the optimized stoichiometry.

References

higher value (about 280 °C) in the Ge rich region. A phase boundary between the Sb-Te phase and the Ge-Sb-Te phase has been clearly identified using synchrotron diffraction.

Refractive index and extinction coefficient were measured at each composition spot using a scanning ellipsometer: some composition ratios were found to have a small extinction coefficient in the amorphous state, a high phase-change temperature, and a large difference in the extinction coefficient between the amorphous state and the crystalline state, suggesting that such compositions can be promising for photonic devices for neuromorphic control. We find that compositions with promising properties are near the boundary between the Sb-Te and the Ge-Sb-Te phases, indicating that co-existence of the phases at microstructural level may be playing a role in giving rise to their properties. This work is funded by an ONR MURI (Award No. N00014-17-1-2661).

2:45 PM BREAK

3:15 PM  EP08.10.05

Rules in van der Waals Epitaxy Fabrizio Arciprete1, 2, Jos E. Boschker1, 3, Stefano Cecchi1, Eugenio Zallo1, Valeria Bragaglia1, 4 and Raffaella Calarco1; 1Paul-Drude-Institute, Berlin, Germany; 2Fisica, Università di Roma “Tor Vergata”, Rome, Italy; 3Leibniz-Institut für Kristallzüchtung, Berlin, Germany; 4IBM Research-Zurich (en dash), Rüschlikon, Switzerland.

Besides graphene, many classes of 2D systems developed over the last few years: group-IV graphene-like Xenes (with X such as Si, Ge, Sn), transition metals dichalcogenides (such as MoS2, WS2, MoSe2, WSe2, MoTe2), III-VI and V monochalcogenides (such as h-BN or InSe, GaS, GaSe, GaTe), and V-VI chalcogenides (V = As, Sb, Bi and VI = S, Se, Te). Sb2Te3 and the pseudobinary alloy GeSbTe exhibit a 2D structure with the size of the building block depending on composition: Sb2Te3 (5 layers), GeSb2Te2 (7 layers), GeSbTe3 (9 layers), GeSb2Te5 (11 layers), etc. The prerequisite for application, as well as for studying the fundamental properties, of such new crystalline materials is the capability of growing high-quality large-area films. Van der Waals (vdW) epitaxy, in which the epitaxy is mediated by weak vdW interactions, represents the way to realize such high-quality films on large scale.

Despite the intense research efforts by many groups toward the vdW epitaxy, a general description of all the phenomena involved is not yet given. In fact, the epitaxial rules for 2D materials are really different from ordinary 3D materials. In 2D epitaxy, the prediction of the phase formed by the vdW heterostructures, the commensurability, the strain relaxation during the interface formation, and the role of the substrate surface reconstructions need to be investigated further.

In this contribution, a general description of the vdW epitaxy will be proposed. We will discuss the epitaxial growth of the 2D GeSbTe alloy deposited by Molecular Beam Epitaxy on the low-mismatched InAs(111) substrates (lattice mismatch ≈1%) for both In- and As- terminated surfaces. The occurrence of the vdW epitaxy is discussed in comparison to other results from literature in order to identify the key mechanisms underlying the process.

3:45 PM EP08.10.06

Growth and Characterization of Epitaxial GeSbTe Films Towards Ge-Rich Compositions Stefano Cecchi, Eugenio Zallo and Raffaella Calarco; Paul-Drude-Institute, Berlin, Germany.

Phase change materials (PCMs) have attracted in the last years the interest of research as concrete candidates for the development of storage class memories. GeSbTe (GST) alloys along the GeSb2Te3 pseudo-binary line are nowadays used as the active material for non-volatile solid-state memories. [1]

For automotive applications, however, higher working temperatures are needed for embedded electronics. This prevents the use of GeSb2Te3 (GST225), which is among (GeTe)x(Sb2Te3)(1-x), compounds the one traditionally employed in PCM memory devices. One strategy to adapt PCM technology to the requirements of automotive applications is to tailor the crystallization temperature and thermal stability of GST by engineering the alloy composition. In this framework, Ge-rich GST alloys have shown increased crystallization temperatures proportional to the excess of Ge. [2]

Here we present a study of epitaxial GST films towards Ge-rich compositions grown by molecular beam epitaxy on Sb-passivated Si(111) substrates. Starting from stoichiometric GST225, the composition of GeSb2Te3 was controlled by increasing the atomic flux of Ge while keeping fixed the other growth parameters. The growth of GeSb2Te3 films was checked in situ by reflection high-energy electron diffraction. We found a gradual loss of crystalline quality with increasing Ge content, possibly related to the deficiency of Te which characterizes the present experiments. The evolution of the composition was studied by X-ray diffraction (XRD) radial scans and Raman spectroscopy. Interestingly, a combination of XRD rocking curves and azimuthal scans provides evidence of stronger in-plane rotational coherence with respect to the substrate, while the material is more prone to form domains misaligned out-of-plane. The characterization of the switching functionality will be carried out.


4:00 PM EP08.10.07

Phase Segregation and Crystallization of Amorphous Ge-Rich GST Alloys Marta Agati1, Daniel Benoit1 and Alain Claverie2; 1CEMES-CNRS, Toulouse, France; 2STMicroelectronics, Crolles, France.

GST alloys have recently been reported to significantly increase the range of working temperatures of PCM memories, an important characteristic to extend their range of potential applications. Moreover, N doping may further increase their endurance and reduce the undesired drift of the low resistance state (crystalline state) upon time. However, the crystallization process i.e., the mechanisms by which amorphous N-doped Ge-rich GST transforms into one or several stable crystalline compounds, is rather unknown. For this reason in this work we report on a systematic study of the structural and compositional changes which affect thin films of amorphous N-doped Ge-rich GST during thermal annealing at various temperatures. The structural evolution was studied using a variety of transmission electron microscopy techniques (HRTEM, SAED, ASTAR), both in-situ and ex-situ, and X-ray diffraction. The chemical composition was analyzed by STEM-HAADF and STEM-EDX.

We show that, during annealing at 380°C, the initially homogeneous Ge-rich GST material locally fluctuates in composition until phase separation occurs while no crystal nuclei are formed. This work is funded by an ONR MURI (Award No. N00014-17-1-2661).

4:15 PM EP08.10.08

Atomic Imaging and Modelling of Bilayers in Hexagonal GST Jianqiing Wang1, Chunlin Ji2, 3 and Wei Zhang1; 1Center for Advancing Materials Performance from the Nanoscale, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, China; 2Peter Grünberg Institute and Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich GmbH, Jülich, Germany; 3The School of Electronic and Information Engineering, State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, China.

Disorder plays an essential role in shaping the transport properties of GeSbTe phase-change materials (PCMs) to enable non-volatile memory applications. Recently, increasing efforts have been undertaken to investigate disorder in the layer-structured GST compounds, especially a special type of swapping bilayer defects. In this work, we focus on hexagonal GST. The samples were prepared by magnetron sputtering and were annealed at 300 oC for half an hour. We thoroughly characterized the structural and chemical features of the major defects in hexagonal GST at atomic scale through chemi-scanning transmission electron microscopy (STEM) experiments. By combining nanoscale density functional theory (DFT) modelling and simulations, we identify that the intermixing of Sb and Te in the bilayers is crucial to stable the defects, and attribute their abundance to the small energy cost. The bilayer defects are demonstrated to be ineffective in altering the electron localization nature but may affecting the quantitative value of electrical resistance in hex-GST.
Devices and Materials to Extend the CMOS Roadmap for Logic and Memory Applications

April 23 - April 25, 2019

Session Chairs: Rinus Lee and John Robertson
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 224 B

10:30 AM *EP09.01.01

Steep-Slope Devices with New Operation Mechanisms for Ultra-Low-Power Applications Ru Huang1,2, Qianqian Huang1,2, Huimin Wang2, Yang Zhao2, Cheng Chen2 and Yangyuwan Wang1,2; 1Key Laboratory of Microelectronic Devices and Circuits (MOE), Peking University, Beijing, China; 2Institute of Microelectronics, Peking University, Beijing, China.

Standby power becomes much more serious than dynamic power with the technology scaling and becomes one critical issue of IC development, particularly for the power constrained applications, such as Internet of things (IoT) and implantable chips which have stringent ultra-low-standby-power requirements. Different from conventional MOSFET, novel device concepts with new operation mechanisms which can achieve ultra-slope subthreshold slope can be found from the conventional thermal limit of subthreshold slope (SS), have attracted immense attention for ultra-low-voltage and ultra-low-power applications. Among all kinds of steep-slope devices, Tunnel FET (TFET) utilizing band-to-band tunneling (BTBT) mechanism and Negative Capacitance FET (NCFET) with ferroelectric (FE) gate are the two of the most promising candidates, with reported demonstrations of their capability of sub-60mV/dec SS at room temperature. However besides the steep SS, the devices need further comprehensive investigation as well as further physical clarification for device design optimization and future circuit applications. TFET devices with the gated p-n structure can theoretically achieve steep SS and ultralow off-state leakage current. However, they face the fundamental low on-current issue due to the relatively low tunneling efficiency. Moreover, it is difficult to obtain high on-current, steep SS and ultralow off-current simultaneously, even adopting narrow bandgap materials. From the perspective of mechanism engineering, a new kind of hybrid operation mechanism of Schottky injection and BTBT is presented, fundamentally addressing the issue of low drive current in conventional TFETs and obtaining higher on-current and lower SS while maintaining ultralow off-current. The proposed multi-finger-gate Schottky barrier TFET (MFSB-TFET) exhibits superior performance with the steep SS of 29mV/decade and large on-off current ratio of >10. The ON-current is improved by 2.5 decades compared with conventional TFET. In addition, the MFSB-TFET also experimentally demonstrates comprehensive electrical properties enhancement in terms of output behavior, capacitance, delay, gain, noise, variability and reliability, showing its great potential for ultra-low-power digital and analog circuits applications. The other possible solution for sub-60mV/dec SS is NCFET. Integrating the FE layer into the gate stack of conventional FET, the voltage amplification effect induced by the NC of FE can lead to the steeper SS than conventional FET without on-current penalty. However, the FE film usually exhibits hysteretic loops of polarization-voltage, and most NCFETs experimentally demonstrate the confliction between SS and hysteresis. Besides, the theoretical explanations of NC effect and hysteresis in NCFETs are still controversial. We present the first direct experimental observation of NC effect in a standalone FE capacitor, proving that the NC is generated from the dynamic polarization switching instead of steady-switching of FE. A new dynamic polarization matching condition is derived and provides new understanding of the steep-slope in the NCFETs. In addition, the physical origin of hysteresis behavior in NCFETs is analyzed, theoretically explaining the SS and hysteresis optimization confliction, which indicates a huge challenge for logic applications of NCFETs. Due to the voltage amplification effect of NC, by further integrating NC to TFET, NC-TFET devices are expected to obtain higher on-current and steeper SS without off-current degradation. A novel NC-TFET design with striped gate configuration is proposed and experimentally demonstrated with sub-60mV SS and nearly non-hysteresis behavior. Benefiting from the hybrid modulation of NC effect and junction depleted-modulation effect, the proposed new NC-TFET design shows great potentials for some standby-power constrained applications.

11:00 AM *EP09.01.02

Negative Capacitance in Ferroelectric Hafnium Oxide Thomas Mikolajick1,2; Uwe Schroeder1, Michael Hoffmann1, Benjamin Max2 and Stefan Slesazeck1,2; 1NaMLab, Dresden, Germany; 2HHM, Technische Universität Dresden, Dresden, Germany.

More than ten years ago, ferroelectric negative capacitance has been proposed [1] to overcome the basic limitations of the voltage scalability in complementary metal oxide semiconductor circuits (CMOS) imposed by the fact that the subthreshold swing cannot be reduced below 60 mV/dec. However, to realize this proposal it was necessary to overcome the massive issues associated with integrating a ferroelectric into a CMOS process [2]. The first report on ferroelectricity in doped hafnium oxide in 2011 [3] therefore quickly turned this idea into a possibly mass manufacturable option for future CMOS scaling. However, although the benefits of voltage amplification achieved by the integration of the ferroelectric into the gate stack can be easily shown using fundamental Landau theory, the possibility of a practical implementation of the effect into CMOS devices is still under discussion in the scientific community. When measuring ferroelectric properties, in general the voltage is forced and therefore the negative capacitance region cannot be observed. Using a series resistor, first indications of negative capacitance could be observed in doped HfO2 [4]. Recently, a pulse measurement technique together with dielectric layer in direct contact to the ferroelectric, finally made it possible to extract the S-shaped curve predicted by Landau theory [5,6]. Already in [1] the idea of introducing a suitable dielectric capacitor in series has been described and used as the basis for subsequent investigations by many groups. However, an important feature of ferroelectrics, namely domain formation, is often neglected in basic simulation work, where Landau theory is used in a way that implies a single domain state [7]. When introducing domains into the theory, it still seems possible to stabilize the negative capacitance region [8]. However, the metal electrode introduced between the dielectric and the ferroelectric in many experimental demonstrations will be detrimental and limit the stabilization to extremely small devices. Coming from the practical side, encouraging data on hafnium oxide based ferroelectrics integrated into state of the art devices have been shown [9], but the connection to the basic material work and theory is often missing. In this presentation the authors will give an overview on their own findings of negative capacitance in hafnium oxide and connect these to literature results on fully integrated devices.

References

A Ferroelectric Semiconductor Field-Effect Transistor
Peide P. Ye; Purdue University, West Lafayette, Indiana, United States.

A ferroelectric semiconductor field-effect transistor (FeFET) was proposed and experimentally demonstrated for the first time. In this novel FeFET, a 2D ferroelectric semiconductor α-InSe$_2$ is used to replace conventional semiconductor as channel. n-In$_2$Se$_3$ is identified due to its proper bandgap, room temperature ferroelectricity, the ability to maintain ferroelectricity down to a few atomic layers and the feasibility for large-area growth. An atomic layer deposited (ALD) Al$_2$O$_3$ passivation method was developed to protect and enhance the performance of the α-InSe$_2$:FeFETs. The fabricated FeFETs exhibit high performance with a large memory window, a high on/off ratio over 10$^4$, a maximum on-current of 671 μA/μm, high electron field-effect mobility with $\mu_{FE} = 312$ cm$^2$/Vs in forward sweep and $\mu_{FE} = 488$ cm$^2$/Vs in reverse sweep, and the potential to exceed the existing Fe-FETs for non-volatile memory applications.

SESSION EP09.02: 2D Materials
Session Chairs: Tony Low and John Robertson
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 224 B

1:30 PM *EP09.02.01
Prospects and Challenges of 2D Materials and Devices
Won Jong Yoo; Sungkyunkwan University, Suwon, Korea (the Republic of).

Two dimensional (2D) materials are being investigated very intensively, some of them holding great promise as emerging semiconducting materials for future nano-electronics, beyond current semiconductor technology which faces hard limitation in performance enhancement due to excessive power dissipation during high frequency operation, while they present ultra-thin body and short channel effect-free state with efficient electrostatic control. These properties enable 2D materials to be very promising candidates that can meet major requirements for high performance memory and logic applications using CMOS and also for electronic and photonic devices operated in emerging future mobile and IoT environment. However, research towards the realization of the 2D materials based CMOS semiconductor devices faces serious challenges which require various innovative technical breakthroughs. In this talk, I would like to firstly address prospects of 2D devices for the future semiconductor applications. Then, I would like to address challenges from the semiconductor device point of view, mainly on crystalline growth of large scale 2D materials, doping of charge carriers into 2D substrates, strong Fermi level pinning from surface defects sensitive material properties, high contact resistance at the interfaces with metal electrodes, and inefficient power dissipation along ultra-thin 2D structures leading to early breakdown.

Acknowledgments: This work was supported by the Global Research Laboratory (GRL) Program (2016K1A1A2912707) and Global Frontier R&D Program (2013M3A6B1078873), both funded by the Ministry of Science, ICT & Future Planning via the National Research Foundation of Korea.

References:

2:00 PM *EP09.02.02
Theoretical Exploration of Energy Efficient Spin Transduction and Switching
Tony Low; Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

There is an intense search for materials that enables energy efficient schemes for charge-to-spin conversion and magnetization switching. I will discuss various proposals in relying on topological effects for the realization of efficient charge-to-spin conversion, such as the Rashba Edelstein effect in topological insulator and the intrinsic spin-Hall effect in topological materials. Next, I will discuss the possibility of magnetization switching via voltage controlled magnetization anisotropy, in ultrathin ferromagnetic layers stacks.

2:30 PM EP09.02.03
2D/3D Semiconductor Heterojunctions of MoS$_2$ and GaN
Michael D. Valentin, 1,2, Matthew Chin, 3, Dmitry A. Ruzmetov, 2, Robert Burke, 2, Kehao Zhang, 2, A G. Birdwell, 2, Masha R. Neupane, 4, 5, Joshua Robinson, 6, Madan Dubey, 6, and Ludwig Bartels; 1, 6 University of California, Riverside, Riverside, California, United States; 2, Sensors and Electron Devices, U.S. Army Research Laboratory, Adelphi, Maryland, United States; 3, The Pennsylvania State University, University Park, Pennsylvania, United States.

A promising approach for high speed and high-power electronics is to integrate two-dimensional (2D) materials with conventional electronic components such as bulk (3D) semiconductors and metals. In this study we explore 2D/3D integration with MoS$_2$ and GaN utilizing vertical heterojunctions to fabricate a 2-terminal device then a 3-terminal bipolar junction (BJT) with novel electronic and optoelectronic properties. Heterojunctions are especially vulnerable to interfacial defects and contamination from transfer processes. Lattice mismatch between MoS$_2$ and GaN has a calculated difference of 1.1% leading to an epitaxial driven growth mechanism. By doping MoS$_2$ during a MOVCD growth process and GaN via MBE, we demonstrate both n-p-n and p-n-p 3-terminal BJTs. We probe interfaces using Raman spectroscopy and cross sectional TEM and confirm our electrical results with I–V analysis.

2:45 PM EP09.02.04
STM Investigation of Graphene/Few-Layer Molybdenum Disulfide Memristor Devices
Jesse E. Thompson, 1, Tanja Roy, 1 and Masa Ishigami, 2; 1 Physics, University of Central Florida, Orlando, Florida, United States; 2 Materials Science & Engineering, University of Central Florida, Orlando, Florida, United States.

Nanoscale mechanisms of memristors and electronic synapses fabricated from vertical graphene/MoS$_2$, van der Waals heterostructures remain largely unexplored. We used scanning tunneling microscopy (STM) and spectroscopy (STS) to investigate the electronic properties of these devices at the atomic scale. We were able to resolve the contributions from defects, specifically to the formation of atomic-scale conductive regions during switching events in these devices. We were also able to induce switching through these devices using the STM tip and to tune the performance of memristors and electronic synapses. We will discuss these results along with theoretical calculations.

3:00 PM BREAK

3:30 PM *EP09.02.05
2D Semiconductor Electronics—Advances, Challenges and Opportunities
Ali Javey; Electrical Engineering and Computer Sciences, University of California, Berkeley, California, United States.

Two-dimensional (2-D) semiconductors exhibit excellent device characteristics, as well as novel optical, electrical, and optoelectronic characteristics. In this talk, I will present our recent advancements in defect passivation, contact engineering, surface charge transfer doping, ultrashort transistors, and heterostructure devices of layered chalcogenides. We have developed a defect passivation technique that allows for observation of near-unitary photoluminescence quantum yield in monolayer MoS$_2$. The work presents the first demonstration of an optoelectronically perfect monolayer. Forming Ohmic contacts for both electrons and holes is necessary in order to exploit the performance limits of enabled devices while shedding light on the intrinsic properties of a material system. In this regard, we have developed different strategies, including the use of surface charge transfer...
doping at the contacts to thin down the Schottky barriers, thereby, enabling efficient injection of electrons or holes. We have been able to show high performance n- and p-FETs with various 2D materials, including the demonstration of a FET with 1nm physical gate length exhibiting near ideal switching characteristics. Additionally, I will discuss the use of layered chalcogenides for various heterostructure device applications, exploiting charge transfer at the van der Waals heterointerfaces.

4:00 PM *EP09.02.06*

**Contact Engineering for 2D Field-Effect Transistors**

Po-Wen Chiu$^1$, Chun-Hao Chu$^1$ and Chao-Hui Yeh$^1$; National Tsing Hua University, Hsinchu, Taiwan; Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

Moving beyond the limits of silicon transistors requires both a high-performance channel and high-quality electrical contacts. The type of barrier at a metal/TMD junction is one of the key issues in TMD field-effect transistors (FETs). It is important to design contacts such that the transmission is dictated by intrinsic properties of the TMD channel rather than by details of the contacts. In this work, we report a systematic study of TMD contacts, with monolayer channel materials WS2 and MoS2 grown by chemical vapor deposition. We show how the contact barrier can be modulated by the work function of contact metals, defects, and contact geometry on a clean surface of TMD. The Fermi level pinning can be effectively mitigated or eliminated through the proper contact engineering. The end-bonded contact, formed through the reaction of transition metals with the TMD channel, exhibited no Schottky barrier and holds great promise for high-performance TMD FETs, enabling future ultimately scaled device technologies.

4:30 PM EP09.02.07

**Reducing Contact Resistances, Unpinning Fermi Levels and Understanding Schottky Barriers**

Yuzheng Guo$^2$ and John Robertson$^1$; Cambridge University, Cambridge, United Kingdom; Swansea University, Swansea, United Kingdom.

A major factor limiting the performance of devices is the contact resistances which depend on Schottky barrier heights (SBHs). Fermi level pinning (FLP) by a high density of states in the semiconductor band gap generally limits the ability to vary the contact work function to minimize the SBH. Recently, it was found that contacts with Bi or Sb between the main contact metal and Si [1] would be less strongly pinned than those with direct contact to Si. To understand the cause of this effect, the SBH of metals on Sb were calculated by DFT. It was found that the low density of states at E_F allows a SB pinning factor S of 0.2 - 0.4, depending on Sb thickness. This suggests that the SBH follows the Fermi Level Theory [2] model where only the density of states at E_F matters. On the other hand, the SBHs of silicones on Si are easier to interpret in terms of the polarization of interfacial bonds (‘Tung model [3]’). This indicates how the control of Schottky barriers, critical to one of the simplest limits to device performance, are still not well understood.


SESSION EP09.03: Poster Session: Devices and Materials to Extend the CMOS Roadmap for Logic and Memory Applications

Session Chairs: Catherine Dubourdieu, Rinus Lee and John Robertson

Tuesday Afternoon, April 23, 2019

5:00 PM - 7:00 PM

PCC North, 300 Level, Exhibit Hall C-E

**EP09.03.01**

**MEMS Process and Characterization for Strain-Engineered 2D Materials**

Edgar Acosta$^1$, Mariana Martinez$^1$, Aldo I. Vidaña$^1$, Sergio Almeida$^1$, Jose Mireles$^1$ and David Zubia$^2$; University of Texas at El Paso, El Paso, Texas, United States; Electrical Engineer and Computer Science, Universidad de California, Berkeley, Berkeley, California, United States; Universidad Autónoma de Ciudad Juárez, Ciudad Juárez, Mexico.

In recent years, an incredible increase in the number of transistors per chip has been observed, which has led to an increasing demand for more power efficient electronics. Additionally, recent studies of two layered materials such as graphene and some transition-metal dichalcogenides (TMDs) have shown strong potential for future use in electronics. One useful property of TMDs is that their electrical and optical properties are highly sensitive to strain. Furthermore, Micro-Electro-Mechanical System (MEMS) can be designed to provide a high level of stress. A low-power switch was recently proposed using a MEMS actuator to strain a MoS2 bilayer with switching energies as low as E < 1.0733 eV [1].

In this work, we present the design and fabrication process of a MEMS-TMD switch designed to provide strain up to 6%. A comb-drive architecture is used for the MEMS actuator. A fabrication process for the MEMS is developed using SiGe technology. Finally, a process to transfer and clamp the TMD onto the MEMS is presented.


**EP09.03.02**

**Application-Driven Perovskite Thin Films with Oxygen Vacancies Controlled**

Prathvek Gopalakrishnan$^1$, Nikoleta Theodoropoulou$^2$ and Ethan C. Ahn$^1$; Electrical and Computer Engineering, The University of Texas at San Antonio, San Antonio, Texas, United States; Texas State University, San Marcos, Texas, United States.

Crystalline metal-oxide thin films are an attractive group of materials for a wide variety of device applications. Among these, the perovskite family of complex oxides have experienced extensive research and development efforts due to their unique multifunctional properties. Despite numerous advances in the field, it is still a challenging task to create a high-quality epitaxial heterostructure on silicon where the intrinsic properties and functionalities of the perovskite oxides are preserved. Additionally, the practical, application-driven methodology to best tune their properties remain relatively unexplored. In this work, these two challenges are addressed by adopting an advanced oxide-MBE technique and controlling the amount or density of the oxygen vacancies, respectively. The flagship perovskite oxide, STO (SrTiO$_3$), was grown directly on top of silicon in an oxide-MBE chamber by co-deposition of Sr, Ti, and molecular O$_2$, and our preliminary analysis indicates that formation of an amorphous SiO$_2$ layer at the interface was well suppressed (ensuring the epitaxy) and oxygen deficiencies (defects) were created inside the STO layer (ensuring tunability). Thotho-step annealing process was applied to control both the crystallinity and oxygen vacancy of the 8.6 nm-thick perovskite thin film. Based on the structural and electrical testing results on the STO/Si heterostructure thin films prepared by oxide-MBE, we propose that STO has great potential to advance the next-generation memory and storage device applications. Its ultra-high dielectric constant (100 to 300) that can be accomplished by eliminating the oxygen vacancies inside the STO layer can significantly improve the EOT for the purpose of developing a high-capacity DRAM. The hysteretic resistance change in the very low operating current regime (a few to a few hundred amperes) suggests that the STO thin film can also contribute to the development of low-power memristor devices.

**EP09.03.03**

**Single- and Double-Gate Synaptic Transistor with a TaOx Gate Insulator and an IGZO Semiconductor Channel Layer**

Keonwon Beom, Paul Yang, Daehoon Park, Minju Kim, Sukni Kim, Hyung Jun Kim, Chi Jung Kang and Tae-Sik Yoon; Myongji University, Yongin, Korea (the Republic of).

To develop brain-inspired neuromorphic computing systems, artificial synaptic devices were investigated using synaptic transistors with single- and double-gate thin-film transistor (TFT) structures. Distinguishable from a two-terminal memristor-synapse, the synaptic transistor enables the synaptic weight to be tuned and then updated by gate biasing during signal processing by drain biasing at the same time. In this study, we demonstrated various synaptic motions with single- and double-gate TFT consisting of an oxygen-deficient TaO$_x$ gate insulator and an indium-gallium-zinc oxide (IGZO) semiconductor channel layer, i.e., an Al-top-gate/SiOx/TaOx/n-IGZO on a SiO$_2$/n-Si-bottom-gate substrate through concurrent changes in gate oxide capacitance, channel mobility, and threshold voltage. This synaptic TFT exhibited the tunable drain current, corresponding to synaptic weight modulation in biological synapse, upon repeatedly applying gate and drain voltages. The drain current modulation features to be analog, voltage-polarity
dependent reversible, and strong with a dynamic range of multiple orders of magnitude (−10^4), as a consequence of the changes in mobility of IGZO channel and gate oxide capacitance, and threshold voltage. The drain current modulation responsive to timing of voltage application emulates synaptic potentiation, depression, paired-pulse facilitation, and memory transition behaviors depending on the voltage pulse amplitude, width, repetition number, and interval between pulses. The synaptic motions could be realized also by double-gate operation that separately tuned the drain current by top-gate bias and sensing it by bottom-gate biasing. It provided the modulated synaptic weight with wide level of synaptic weight with respect to read condition using bottom-gate stack without read-disturbance. It demonstrated an operation scheme that the signal processing can be performed using the bottom-gate biasing during simultaneous updating of synaptic weight with the top-gate biasing. In addition to the application of this synaptic TFT to artificial synapse for neuromorphic system, its analog, reversible, and nonvolatile changes in drain current as a result of gate biasing can be applied to the operation for nonvolatile memory and field-programmable logic devices.

EP09.03.04 Multiscale Modeling Framework for 2D-Material MOS Transistors Madhusudhana Ibrahma and Santanu Mahapatra; Centre for Nanoscience and Engineering, Department of Electronic Systems Engineering, Indian Institute of Science, Bangalore, Bangalore, India.

Atomically thin 2D materials have ushered in a new era in the field of materials science and has been translated to notable advancements in the design of sensors, optoelectronic devices, flexible electronics [1]. These atomically thin materials are predicted to replace conventional bulk materials, Si and Ge, for transistor channels and extend the complementary metal oxide semiconductor technology roadmap beyond the ultimate scaling limit [2]. Constant efforts are being made to synthesize devices based on some of the recently discovered van der Waal's materials such as graphene, hexagonal boron nitride, MoS_2, phosphorene [3,4,5]. Density functional theory (DFT) calculations have suggested a large number of 2D materials and their derivatives for device applications [6]. In order to narrow down the material and design selection space for time- and cost-heavy experimental device fabrication, atomic level DFT calculations need to be coupled with device-level physics models. Thus, starting from first principles DFT calculations, we propose a multiscale computational framework to extract important electronic parameters, such as effective mass, band gap, real and complex band dispersion, and phonon dispersion for various materials and their potential application in electronic and optoelectronic devices.

References:

EP09.03.05 Suppression of Defects at High-K/SiGe Interface with Monolayer Si ALD Deposition Harshil Kashyap1, Mahmut Kavrik1, Victor Wang2 and Andrew Kummel1; 1Material Science, University of California, San Diego, San Diego, California, United States; 2ECE, University of California, San Diego, San Diego, California, United States; 3Chemistry and Biochemistry, University of California, San Diego, San Diego, California, United States.

High mobility SiGe is promising for p-channels in CMOS. Successful integration of SiGe into CMOS necessitate low defect SiGe/gate oxide interfaces for practical device operation. The existence of Ge on SiGe surface is problematic as it forms GeOx during gate oxide deposition and induces defects at the interface. Selective oxidation of Si is challenging especially during ALD deposition at elevated temperatures. In this study, a novel method to form low defect interface is demonstrated to deposit monolayers of Si on SiGe with plasma assisted ALD. In this method, HF cleaned SiGe wafer is subjected to 2 super cycles of SiCl_4 and Ar:H_2 downstream plasma at high temperature (350°C). Hydrogen atoms from the Ar:H_2 plasma interact with SiCl_4 on the SiGe producing Si(s) and HCl(s). HCl desorbs from the surface at high temperature and is purged out. This leaves behind one monolayer of Si(S). This step is followed by N_2:H_2 downstream plasma to help passivate the interface. The downstream plasma operates at high pressure (~100 torr) which ensures negligible ions flux thereby preventing ion induced defect formation. It is hypothesized that N_2:H_2 downstream plasma results in Si-N, Si-H, and N-H bond formation and SiNx prevents outdiffusion of Ge while Si and N-H forms a good nucleation layer for subsequent gate oxide ALD. Experiments with Al,O_3, HfO_2; and ZrO_2 ALD gate oxide deposition after this Si monolayer deposition and N_2:H_2 downstream plasma passivation show up to 50% decrease in interface defect density; for example with approximate 5 nm ZrO_2 gate oxide deposition, the Dit = 1.0 x 10^{12} eV/cm^2 compared to samples with monolayer of Si (~ Dit = 1.9 x 10^{12} eV/cm^2) and compared to samples with just HF treatment (~ Dit = 3.6 x 10^{12} eV/cm^2).

EP09.03.06 Development of a Hierarchical Process for Optimization of the Design for MEMS Vibrating Ring Gyroscope for Miniaturized Space Attitude Control System Daniel Choo1, Ibrahim Ellalde, Muneera Al Shabab and Wajih Syed; Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates.

Micro-electromechanical systems (MEMS) inertial sensors are expected to enable so many emerging military and commercial applications that they are becoming too numerous to list. MEMS is probably the most exciting new inertial sensor technology ever and development is a worldwide effort. Apart from size reduction, MEMS technology offers many benefits such as batch production and cost reduction, power (voltage) reduction, ruggedness, and design flexibility, within limits. However, the reduction in size of the sensing elements creates challenges for attaining good performance. In general, as size decreases, then sensitivity (scale factor) decreases, noise increases, and driving force decreases. Currently, the performance of MEMS IMUs continues to be limited by gyro performance, which is now around 5-30°/h, rather than by accelerometer performance, which has demonstrated tens of μg or better.

In this study, we develop an innovative, affordable, miniature, low-power, navigation-grade integrated gyroscope for the attitude control system that applies MEMS technology to a variety of applications including, but not limited to, navigation, stabilized platforms, and field programmable logic devices.

EP09.03.07 Influence of Intermixing on Perpendicular Magnetic Anisotropy of Ion-Beam-Deposited CoFeB MTJs for STT-RAM Tania Henry1, Narasimhan Srinivasan2, Katrina Pietruski1, Vincent Ip3 and Frank Cerio1; 1Veeco Instruments Inc, Plainview, New York, United States.

The interface of CoFeB with MgO that forms a Magnetic Tunnel Junction (MTJ) is a critical element of Perpendicular Magnetic Anisotropy (PMA) in STT-RAM devices. The TMR and RA product, which is a key figure of merit for these devices, is very sensitive to the quality of this interface. Intermixing and wettability of the CoFeB on MgO are two critical parameters that are of interest in evaluating this interface. In this work we report the fabrication of MTJ stacks and characterization of this interface. Ion Beam Sputtering (IBS), a very low rate deposition process in which one can control both energy and angle of deposition, is used to fabricate these MTJ structures. We probe intermixing by estimating the magnetic dead layer (MDL) of a stack using magnetic measurements and report a MDL of 0.2 nm after annealing the MTJ stacks at a temperature greater than 300
Role of Hypochlorous Acid in Solution-Processed P-Type Oxide Thin-Film Transistors for Oxide Semiconductor-Based CMOS Logic

Tae Sook Jung, Heesoo Lee, Hee Jun Kim, Jin Hyeok Lee, Hyun Jae Kim and Jusung Chung; School of Electrical and Electronic Engineering, Yonsei University, Seoul, Korea (the Republic of).

Amorphous oxide semiconductor thin-film transistors (TFTs) have achieved enough technological advances to be applied to mass-produced display products. However, the technological development of the oxide TFTs is limited to n-type, and only a few researches on p-type oxide TFTs have been reported due to the lack of p-type oxide materials and rigorous fabrication conditions. Furthermore, since p-type oxides have many localized states near the valence band maximum, it makes control of the amount of metal vacancy, which is the origin of the hole carrier, difficult. Due to the above issues, researches on p-type oxide TFTs have become increasingly challenging. Nevertheless, researches on p-type oxide TFTs are essential due to a demand on oxide semiconductor-based complementary metal oxide semiconductor (CMOS) logic circuits.

Herein, we propose a simple method to enhance the switching characteristic of the p-type copper oxide (CuO) TFTs via the oxidation effect of hypochlorous acid (HClO). HClO is a relatively inexpensive material to manufacture by reacting chlorine gas with water, and a useful oxidant because of generating oxygen radical (O*), one of the strong reactive oxygen species with heat or light conditions. Because of this radical-generating property, HClO is widely used in the fields of sterilization, disinfection, and bleaching in industry. In this study, the HClO treatment was carried out to optimize the hole carrier concentration through the suppression of the copper vacancy (V_{Cu}) in the CuO thin film. Also, we investigated the effects of O* on the CuO thin film generated from HClO, and the variations of chemical composition were verified by chemical analysis. Through the robust oxidation by HClO, the amount of Cu-O bonds increased and the amount of V_{Cu} acting as the origin of hole carriers decreased within the CuO. In the modified CuO TFT, the superior switching characteristic was achieved with the subthreshold swing of 0.70 V/dec., the on/off current ratio of 4.86 \times 10^{4}, and the field-effect mobility of 2.83 \times 10^{-3} cm^{2}/V\cdot s, while pristine CuO TFT did not show switching characteristic.


GeSe/GeSe-M (M = Sn, Al, Ti, W, Cr, Pb, Cu, C)-Based Optically-Gated Transistor—M Influence on Optical and Electrical Properties

Md Faisal Kabirj, Randall Bassine and Kristy A. Campbell; Electrical and Computer Engineering, Boise State University, Boise, Idaho, United States.

Electronic devices made with alternating layers of undoped and doped chalcogenide materials, Ge_{2-x}Se_{x}/Ge_{2-x}Se_{x}-M (M = Sn, Al, Ti, W, Cr, Pb, Cu, C) exhibit transistor-like current-voltage (I-V) curves when illuminated. These devices, referred to as optically-gated transistors (OGTs), have two electrodes: a source and drain. Current is measured between the source and drain electrodes when the chalcogenide material (which acts as a ‘gate’) is illuminated. In this work, the effect of the metal dopant on the transistor characteristics are measured. The transistor materials are characterized using UV-Vis to explore the band gap and electronic structure. Raman spectroscopy is used to verify incorporation of M into the Ge_{2-x}Se_{x} material. Photoconduction is investigated using electrical characterization as a function of wavelength, light intensity, and temperature. The devices were tested from 385 to 1260 nm and were operational over that entire range.

The metal dopant is shown to clearly influence the transistor optical responsivity, maximum current, threshold voltage, electrical switching speed, and optical band gap. A transistor fabricated with M = Al is demonstrated in three applications: as an access transistor to a memristor memory element, voltage control of an optically addressed optical amplifier; and in an optical wavelength converter circuit.

MoTe_{2} p-n Junction Formed via Edge Contact and Oxidation

Changseik Kim and Won Jong Yoo; Sungkyunkwan University, Suwon-si, Korea (the Republic of).

MoTe_{2} is a promising two dimensional material due to phase transition and ambipolar transport with a band gap of 1.0 eV.[4] But MoTe_{2} is sensitive to environment and easy to oxidize.[5] Here, we demonstrated one-dimensional edge contact to MoTe_{2} covered with h-BN passivation layer and etched by SF_{6} plasma. The Schottky barrier height of edge contact is found to be 0.01-0.03 eV for various metals (titanium, chromium and palladium). Additionally, MoTe_{2} edge contact with h-BN passivation shows good stability under ambient environment and oxygen plasma. But MoTe_{2} without h-BN passivation layer is oxidized and changed to strong p-type. Based on the n-type characteristics from edge contact and p-type characteristics from oxidation, we were able to fabricate MoTe_{2} p-n junction with a rectifying ratio of 10^{4}.


This work was supported by the Global Frontier R\&D Program (2013M3A6B1078873) at the Center for Hybrid Interface Materials (HIM), both funded by the Ministry of Science, ICT & Future Planning via the National Research Foundation of Korea (NRF).

Nonvolatile Capacitance Changes in Metal-Oxide-Semiconductor Device with Resistive Switching Floating-Gate Structure for Nonvolatile Memory and Programmable Logic Device Application

Minju Kim, Daehoon Park, Keonwon Beom, Paul Yang, Sunki Kim, Hyung Jun Kim and Tae-Sik Yoon; Myongji University, Yongin, Korea (the Republic of).

Nonvolatile capacitance changes in metal-oxide-semiconductor (MOS) device with floating-gate structure by resistive switching through filament formation were investigated for the application to nonvolatile memory and programmable logic devices. In general, the electrical charging of the floating-gate located inside the gate oxide has been utilized to shift the threshold voltage for nonvolatile memory and programmable logic devices. However, the approach to use the threshold voltage shift by electrical charging has faced difficulties in further scaling due to undesirable cell-to-cell crosstalk. Instead of using the electrical charging of floating-gate, the device performance such as drain current, threshold voltage, and transconductance can be altered by changing the capacitance of gate oxide. In this study, we demonstrated the change of gate oxide capacitance in MOS device with floating-gate structure, i.e., an Ag-control-gate/CoO_{2}/Pt-floating-gate/HfO_{2}/n-Si substrate, where the formation of conducting filament in Ag-control-gate/CoO_{2}/Pt-floating-gate stack by voltage application increased the gate oxide capacitance as reducing the effective oxide thickness. For example, the accumulation capacitance corresponding to the serial capacitance of CoO_{2} and HfO_{2} was increased considerably from ~40 pF before applying positive programming voltage in Ag-control-gate to ~55 pF after applying the voltage while preserving the typical shape of capacitance-voltage curve. The increase of capacitance was induced by the voltage-driven migration of Ag ions through CoO_{2} layer, leading to the formation of filament between Ag-control-gate and Pt-floating-gate and subsequent reduction of effective thickness of gate oxide. In contrast, the reference device with a structure of an Al-control-gate/CoO_{2}/Pt-floating-gate/HfO_{2}/n-Si did not exhibit the increase of capacitance because Al atoms did not migrate through CoO_{2} layer. Instead, it showed little decreased capacitance as increasing voltage possibly due to the migration of oxygen ions from CoO_{2} to Al-control-gate that reduced the relative permittivity of CoO_{2}. Since the gate oxide capacitance could be changed by programming voltage applied to control-gate, which subsequently changes the threshold voltage and drain current, it could be applied for nonvolatile memory and programmable logic devices without the use of electrical charging in floating-gate. These results demonstrated the novel scheme of memory and logic device operations through the change of gate oxide capacitance through resistive switching by filament formation in floating-gate MOS device structure.

Influence of Bulk/Interface Anomalies Upon Resistive Switching in Dual Ion Beam Sputtered ZnO Based Memristive Devices

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In this work, we report the effect of interface anomalies such as disorder-induced interface states, Schottky barrier formation/dissolution for a resistive switch or memristor. Distribution of bulk defects with applied bias governs switching and also attributes to formation/dissolution of interfacial oxide. The present work considerably contributes to...
further understand the conduction mechanisms of a wide range of resistive switches. 

Al/ZrO/Al (AZA) device depicts forming-free bipolar resistive switching with memristive behavior [1]. Bipolar against Unipolar resistive switching [2] is attributed to formation/dissolution of Schottky barrier. To further understand the effect of various other interface anomalies, we performed CV characterization of device in HRS and LRS states for different frequencies. As we can observe from Fig. 1(a), we may observe higher capacitance at a lower frequency which denote the presence of trap charges in bulk as at lower frequencies trap charges also make significant contribution to total capacitance. Further, we can also observe from CV characteristics of device for device in HRS and LRS at 1 MHz in Fig. 1(b) that for device in LRS and near SET voltage, the thickness of the oxide barrier reduces to minimum which leads to set device into LRS and hence total capacitance increases to maximum. As we vary the voltage and it comes near RESET voltage, the thickness of the oxide barrier will increase to its maximum and device will set into HRS and hence total capacitance will decrease to minimum. Fig. 2 (a) shows the I-V characteristics of AZA device. The device AZA shows excellent repeatability for 250 set/reset cycles (Fig. 2(b)).

We believe our work could play a crucial role in further understanding of conduction mechanism of resistive switching devices in the future.

Acknowledgement: Authors are thankful to Sophisticated Instrument Centre (SIC) of IIT Indore for DBBS facility. Mangal Das and Gaurav Siddarth would like to thank Ministry of Electronics and Information Technology (MeitY), Government of India, for providing fellowship under Visvesvaraya PhD Scheme for Electronics and Information Technology (IT). Amithesh Kumar would like to thank Council of Scientific and Industrial Research (CSIR) for providing fellowship. Prof. Shaibal Mukherjee is thankful to MeitY for the Young Faculty Research Fellowship (YFRRF) under the Visvesvaraya PhD Scheme for Electronics and IT.

EP09.03.13 Impact of Metal/Semiconductor Junctions in the Resistive Switching of Yttria Based Memristive System Mangal Das, Amithesh Kumar, Sanjay Kumar, Biswajit Mandal, Pawan Kumar and Shaibal Mukherjee; Indian Institute of Technology, Indore, India.

In this work, self-directed channel (SDC) memristor devices [1] with a Sn-Ch layer (Ch = O, S, or Se) were fabricated and electrically characterized in order to determine the role of the chalcogen atom in the memristor properties. The SDC device structure is a sandwich structure consisting of the following layers (from bottom to top electrode): W/GeO/Sn-Ch/GeO/Ag/GeO/W. The device is fabricated by depositing all layers via in-situ sputtering. The final W electrode layer effectively caps the device.

Current-voltage (I-V) curves of the devices were obtained. The I-V curves were analyzed to study the conduction mechanisms of each device type. This includes the analysis of Schottky emission, Space-charge limited Conduction [2], and Poole-Frenkel emission [3]. In addition, the first and second write threshold voltage of these devices are compared. The response of each device type to a sinusoidal input signal was also measured and used to classify the memristor type [4].

References:

EP09.03.15 Enhancement of Electrical Properties for Black Phosphorus Using the via Contacts Embedded in h-BN Myeongjin Lee and Won Jong Yoo; Sungkyunkwan University Advanced Institute of Nano-Technology, Sungkyunkwan University, Suwon-si, Korea (the Republic of).

Black phosphorus (BP), one of the allotropes of phosphorus, is a promising candidate for future nano-electronics and nano-photoelectronics. Unlike conventional two dimensional semiconductor materials which show n-type property and high electron mobility, BP shows p-type property and high hole mobility [1]. However, BP faces limitations in application to future electrical devices since BP is easily degraded in air atmosphere, and therefore studies to prevent BP from being oxidized in air atmosphere are required. Here, we suggested a via method for suppressing degradation of BP, which uses metal embedded hexagonal boron nitride (hBN) on BP. The fabricated devices showed good electrical properties because of the suppression of degradation of BP. The devices also showed low contact resistance since ultra clean surface between metal and BP was formed. Furthermore, through the applying force between metal and BP by atomic force microscopy (AFM) probes, the performance of the devices were increased because contact between metal BP become better.


Acknowledgements
This work was supported by the Global Research Laboratory (GRL) Program (2016K1A1A2912707) and Global Frontier R&D Program (2013M3A6B1078873), both funded by the Ministry of Science, ICT&Future Planning via the National Research Foundation of Korea (NRF).
One of the most prominent features of the ferroelectric domain walls (DWs) is their electrical conductivity, which was observed in a number of ferroelectric materials, such as BiFeO$_3$, Pb(Zr,Ti)O$_3$, ErMnO$_3$. Here, we combine scanning transmission electron microscopy (STEM) and local probe techniques to investigate the conducting properties of the charged DW in the ion-sliced single-crystalline LiNbO$_3$ thin films with sub-$\mu$m thickness. STEM shows large inclination of the electrically-generated 180° DWs away from the polar z-axis (with inclination angles reaching 16°) suggesting that these DWs are strongly charged. Atomic column STEM imaging reveals the dipolar-kinked configuration of the Nb atoms along the inclined DWs. By using piezoresponse force microscopy (PFM) in combination with conductive atomic force microscopy (CAFM) performed both on z- and x-cut surfaces, it was shown that head-to-head DWs exhibit much higher conductivity than the tail-to-tail DWs, suggesting an electronic type of conductance. One of the most important findings is a possibility of DW conductivity modulation by an external voltage. It is demonstrated that the resistance of the LiNbO$_3$ thin film capacitors can be changed continuously by 5 to 9 orders of magnitude by controlling the DW perimeter allowing development of multi-level resistive switching devices. Resistance states can be altered by exposure to cumulative voltage pulses (resistance plasticity), suggesting that these domain wall memristors might be useful in the context of artificial synapses.

**EP09.03.17**

Transport Analysis of 4H-SiC Power Devices Using Full-Band Ensemble Monte Carlo Method Chi-Yin Cheng and Dragica Vasileska; Arizona State University, Tempe, Arizona, United States.

Energy issue is one of the most important things for us human kind. Therefore, we need an accurate and reliable model to help us develop and design the power devices. For this purpose, being one of the most promising materials for high power applications, 4H-SiC will be investigated in detail for improving performance of existing technology using in-house full-band Monte Carlo device simulator that is a subject of this work. The commercial TCAD tools are always based on effective mass approximation, however, most of the power electronic devices are operated under high electric field, so the non-parabolic band approximation cannot hold anymore. Hence, we need full-band analysis.

First ingredient in the process of building a device simulator is calculation of the band structure. In that respect, the empirical pseudopotential method (EPM) provides an effective way to get the band structure since we can adjust parameters to fit measurements (optical gaps). Here we refer to findings of G. Ng et al. to re-build the band structure. 205 eV cut-off energy was adopted; hence 527 plane waves were considered. The first Brillouin zone in reciprocal space of 4H-SiC is hexagonal. The full band structure of 4H-SiC is calculated, the indirect band gap is found to be 3.246 eV and is between $\Gamma$ point and M point. It is quite close to the commonly known value of 3.26 eV.

Next task in the sequence is the calculation of the scattering rates for which a Density of States (DOS) function is needed. The most widely used method for DOS calculation was proposed by Gilat and Raubenheimer in 1966. They extended the original method in 1967 also to hexagonal close-packed crystals. The first step in the DOS calculation is to discretize the k-space into smaller volumes. We only consider the irreducible wedge, which is 1/24 of the first Brillouin zone, because of symmetry. The wedge can be discretized into rectangular meshes and smaller wedge meshes. If we assume that linear extrapolation works good in every mesh, then the intersections of constant energy surfaces inside meshes are replaced by parallel planes $S(k, n)$ which are perpendicular to the gradient $\nabla f(E(k, n))$. If $w$ is the distance of a particular energy plane from $k$, inside a mesh, the range $w$ determines the possible cross-section area $S(k, n)$. $L_n$ are defined as $L_n = \lambda_{\text{free}}$. We rearrange them in a decreasing sequence $L_1 \geq L_2 \geq L_3 \geq 0$. All possible $S(k, n)$ for both rectangular meshes and smaller wedge meshes are found. After calculating all cross-section area and relating equations, we obtain the DOS function.

Once the DOS function is calculated, to analyze 4H-SiC devices, we have to consider acoustic, non-polar optical and optical phonon scattering. Thus, we create a scattering table using the information from the DOS. For the typical doping level in 4H-SiC device applications, the Brooks-Herring model is not valid. Hence, both electron-electron and electron-ion interactions are calculated. To save the runtime, we use the particle-particle-particle-mesh (P³M) method to get an efficient analysis procedure. The P³M divides the Coulomb force into two parts, the short-range force and long-range force (mesh force). We only need to consider the short-range forces for the carriers and ions close to the carrier we are tracing during each time step; the long-range force will be included via the solution of the 3D Poisson's solver.

We present at the conference simulation results of a N+-n-N+ resistor from where we extract the results for the low-field electron mobility dependence upon Coulomb in 4H-SiC devices, and the high-field electrons behavior where band structure effects are important.

**EP09.03.18**

Fabrication of Ferroelectric V-Doped ZnO Films Fabricated via Sol-Gel Method Woo Jun Seol, Hyun Jin Joh, Jun Young Lee, Tae Yoon Kim and Ji Young Jo; Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Zinc oxide, which has high exciton binding energy (60mV) and a wide band gap (3.73eV)[1], is widely used for optoelectronic devices, piezoelectric sensors and actuators, and for non-volatile memories. Furthermore, ZnO-based ferroelectric materials have been intensively studied for a non-toxic, high temperature ferroelectric applications. While dopants such as Ca,Fe are suggested to induce ferroelectricity of ZnO films[2], especially Vanadium(V)[1], which has smaller ion radius than Zn, induces off-centered behavior of ZnO lattice and relatively larger remnant polarization. These metal-doped ZnO films have been fabricated with Pulsed Laser Deposition, sputtering, etc. However, these methods are high-cost and have difficulties in large-scale process at device scale. We used sol-gel method for fabrication to overcome these drawbacks. Higher crystallinity is needed to induce larger remnant polarization of the film, which could be controlled by elements such as deposition, preheating conditions. Here, we suggest dopant concentration and annealing condition to induce higher crystallinity of V-doped ZnO film via sol-gel method.

In this work, zinc acetate dihydrate (Zn(CH$_3$COO)$_2$•2H$_2$O) and vanadyl acetylacetonate (C$_{9}$H$_{9}$O$_{5}$V) were dissolved in 2-methoxyethan with 2-dimethylaminoethanol (C$_{9}$H$_{11}$NO) as a stabilizer at 75°C for 2 hours on a hot plate to make a solution for sol-gel method. The 200 nm-thick V-doped ZnO film was deposited using spin-coating and preheating and annealing to induce higher crystallization of film. The Pt top electrodes with a thickness of 30 nm were deposited using an electron beam evaporator to form capacitor structures.


**EP09.03.19**

Manipulating the Electrochemical Metalization Cell Kinetics by the Anion Electrode and Tunable Electrolyte Ziyang Zhang, Yao Yuan Wang, Huanglong Li and Luping Shi; Tsinghua University, Beijing, China.

Electrochemical metallization (ECM) memories have the potential to replace today's technology, enabling novel memory and computing architectures circumventing the von Neumann bottleneck. Typically, the operation of ECM cell is based on the electrochemical redox reactions of the cation supplying active electrode. However, the possibility of utilizing new materials for the active electrode remains largely undiscovered. In addition, the ECM cell kinetics are strongly determined by the electrolyte, which can hardly be altered after the cell has been fabricated. Therefore, it is necessary to investigate the influence of the electrode and electrolyte on the ECM cell kinetics. In this work, we engineer the anion supplying active electrode and tunable electrolyte into the electrochemical metallization cell. First, to investigate the electrode dependent switching characteristics of the ECM cells, we fabricate the ECM cell with Te as active electrode. It is found that the SET operation of the device occurs under negative voltage on the active electrode. This behavior is opposite to that of the device with Ag electrode, indicating that Te supplies anions by the ECM mechanism. Different modes of switching between the two types of
cells, namely, unipolar switching for Pt/GeS/Te cell and bipolar switching for Pt/Ge2Sb2Te5/GST/Te cell are observed. These phenomena can be attributed to the rupture of the film by Joule heating for the former and by ECM for the latter in the RESET process. Next, we fabricate the ECM cell with solid phase tunable GST electrolyte to investigate the electrolyte dependent switching characteristics of the ECM cells. The resistive switching characteristics of the cells with different GST phases are examined. The magnitude of the high resistance, the SET voltage and the on/off ratio are found to be considerably affected by the solid phase of GST, whereas the magnitude of the low resistance is least affected. Moreover, a transition from volatile to nonvolatile SET switching is only observed for crystalline GST based cell under prolonged voltage sweep, but not for amorphous GST based cell. This work provides a springboard for more studies on the manipulation of the ECM cell kinetics by tunable electrode/electrolyte and the resulting unprecedented device functionalities.

EP09.03.20

Bidirectional and Multilevel Threshold Switching of Ag-Dielectrics Diffusive Devices for Neuromorphic Computing Applications Yaoyuan Wang1,2,3, Ziyang Zhang1,2,3, Shuang Wu1,2, Lei Tian1,2,3, Huaqiong Li1,2 and Luping Shi1,2,3. 1Department of Precision Instrument, Tsinghua University, Beijing, China; 2Center for Brain Inspired Computing Research, Tsinghua University, Beijing, China; 3Beijing Innovation Center for Future Chip, Tsinghua University, Beijing, China.

Non-volatile memristor crossbar arrays have great potential in brain inspired computing and next generation high-density memories. Diffusive devices with volatile threshold switching (TS) behavior, which are based on the phenomenon of spontaneous rupture of filaments in dielectrics, are of importance in selector applications to suppress the sneak current issue of memristor arrays. Besides, their rich synaptic dynamical behaviors can also enable novel designs in neuromorphic computing to extend the circuits based on the complementary metal-oxide-semiconductor. In this work, we have realized reproducible bidirectional and multilevel TS behavior on Ag-dielectrics diffusive devices. The ON/OFF ratio and the OFF current of the device TS behavior are ~10^4 and ~10^2 A, respectively, which are suitable for selector applications. And we also realize stochastic and multilevel TS by optimizing the device structures. For neuromorphic applications, we integrate the stochastic TS into the stochastic learning process of deep neural networks, and demonstrate the multilevel TS into short-term and long-term plasticity for electronic synapses. Simulations of nanoparticles diffusion are also carried out to study the mechanism of this bidirectional and multilevel TS process. The simulations show that these phenomena are mainly caused by the diffusion and redistribution of Ag nanoparticles. This work illustrates that Ag-dielectrics diffusive devices are promising candidates for neuromorphic computing applications.

EP09.03.21

Optoelectronic CMOS Transistors—Performance Advantages for Sub-7nm ULSI, RF ASIC, Memories and Power MOSFETs James Pang; Advanced Enterprise and License Company, Linthicum, Maryland, United States.

Substantial increase of output current, and Ion / Ioff ratio, for sub-7nm low power CMOS transistors can be accomplished using a novel optoelectronic technology, which is 100% compatible to existing CMOS process flow. For RF or mixed signal ASICs, adding photonic components may improve the cut-off frequency, and reduce series resistance. Products that utilize power regulating devices, such as power MOSFETs, will benefit from the optoelectronic configuration to achieve much lower Ron and high avalanch breakdown voltage at the same time. For semiconductor memories, including DRAM or FLASH, the photonic technique may reduce the ERASE / WRITE / access time and improve the reliability.

Photon generating and sensing devices can be integrated in the drain region of a MOSFET, FINFET or power MOSFET as one transistor. The laser diode is turned on only when the MOSFET is switched to on. The laser is off when the MOSFET is switched off. When both laser and MOSFET are on, light is absorbed by the APD ( Avalanche Photo Diode), which is fabricated in the drain / well regions of the MOSFET, and generates avalanche breakdown currents as part of the output drain current. In this paper we will discuss how to implement this optoelectronic technique for low power, high speed sub-7nm CMOS, memories (DRAM, SRAM, FLASH), and high power MOSFETs.

Sub-7nm CMOS Transistors. Process integration of a laser in the drain region of a MOSFET or FINFET may be simplified. Cross section of an optoelectronic MOSFET shows device configuration, where part of the drain is etched and redeposited with laser films. An equivalent circuit of the device provide step-by-step detailed operations. Please notice that if the substrate is silicon, the laser films ( direct band gap materials) can be deposited selectively on silicon through low temperature epitaxy. If the substrate is GaAs, or other compound semiconductor, a thin silicon film may be deposited on the compound substrate. MOSFET is build in the top thin silicon film, and laser is formed on the compound substrate after selective etching of silicon.

Similar integration techniques can be applied to FINFETs, with low temperature selective epitaxy of lasing semiconductor films in the drain area of a FINFET. The fin can be silicon or GaAs. If the fin is GaAs, a thin silicon epi layer needs to be deposited on GaAs, then selectively removed right before the lasing films are deposited.

In order to further simply the process integration, it is feasible to integrate the laser in the contact 1 or via between metal 1 and silicide. Improvement of MOSFET output current depends on external quantum efficiency and the APD absorption rate. To achieve optimized CMOS drive current, high laser quantum efficiency and APD absorption rate are needed.

Power MOSFETs. Cross section of a discrete vertical power MOSFET illustrates how a laser diode is integrated. For this type of devices, the drain is located in the back side of the chip. Source is on the top of the chip. Deposition of compound laser semiconductor films in the back side of the chip creates a laser. When a high voltage is applied to the drain, a large depletion region is formed along the drain junction in order to sustain a high breakdown voltage. High-intensity light is produced from the laser in the backside, and absorbed in the depletion region to produce light current, which reduces Ron.

Nonvolatile Memories: SRAM, DRAM, FLASH, SONOS, EEPROM – Light Assisted Very High Speed Operations. An optoelectronic Flash memory is a SONOS memory (NOR Flash) with a laser integrated in the drain area. For the Write operation, typically with hot carrier injection, a gate voltage is applied to turn on the word line transistor, and a drain voltage is applied to turn on the laser – light is produced and absorbed in the depletion regions in the channel and drain. Hot carrier injection is enhanced by the light current, and the Write operation is much faster.

EP09.03.22

Atomic Force High Frequency Phonons Nonvolatile Dynamic Random-Access Memory Compatible with Sub-7nm ULSI CMOS Technology James Pang; Advanced Enterprise and License Company (AELC), Linthicum, Maryland, United States.

This paper reports a novel low power, fast nonvolatile memory utilizing high frequency phonons, atomic force dual quantum wells, ferromagnetism, coupled magnetic dipoles and CMOS-based magnetic devices. Random access is accomplished with the magnetic fields generated from ring-gate MOSFETs. Very high-speed memories, such as SRAM and DRAM, are mostly volatile (data are lost when power is off). Nonvolatile memories, including FLASH and MRAM, are typically not as fast as has DRAM or SRAM, and the voltages for WRITE/ERASE operations are relatively high. This paper describes a silicon nonvolatile memory that is compatible with advanced sub-7nm CMOS process. It consists of only one transistor (MOSFET) – small size, and more cost effective, compared with a 6-Transistor SRAM. There is no need to refresh, as required by DRAM. The access time can be less than 1ns – close to the speed level of relaxation time - much faster than traditional FLASH memories and comparable to volatile DRAM. The operating voltages for all memory functions can be as low as high speed CMOS.

A fast non-volatile dynamic random access memory is different from NAND Flash, for which random access is not possible, and NOR Flash, which is relatively slow and high operation voltages are required. Traditional MRAM (Magnetic Random-Access Memory) uses the material properties of magnetic films, which might not be reliable after many operational cycles. A magnetic nonvolatile DRAM (MNV-DRAM) consists of a main gate on top of a silicon substrate with implanted source and drain regions, a floating phonon gate above the main gate, and a control gate above the phonon gate. In between the gates there are vacuum gaps of a few Å. The floating phonon gate consists of polarized ferromagnetic thin films. The control gate is made of a conducting layer on top of a ferromagnetic thin film. The main gate is made of a ferromagnetic thin film on top of a conducting layer. The ferromagnetic films in the phonon gate are implanted with positive or negative charges. As the result, there is an electro-magnetic field with dual quantum wells in between the control and main gates from atomic forces, where the floating phonon gate switches from one quantum well to the other with very high frequency. The layout
design of the 3 gates may be rectangular, or circular (3 loops on top of each other), in order to achieve random access with magnetic fields from the currents in the loops. Due to the currents flowing in the loops, magnetic fields from each loop couple with each other, forming two magnetic dipoles. Motions of the loops depend on the polarity of the dipoles. When currents flow in the same direction, there is an attracting force between the two loops. If currents flow in opposite directions, there is a repelling force. The channel length of the ring gate MOSET is approximately the length of the ring, as described by a cross section (cut along the ring). If the device is cut across the ring, this shows the width of the MOSET.

Conclusion: A novel atomic force magnetic nonvolatile memory is presented in this paper. Nonvolatile functions are achieved by high frequency phonons and quantum wells. Random access is accomplished with coupling of magnetic dipoles. This type of memory requires very low voltages for Write / Erase / Read operations and no Refresh is necessary. The speed is much higher than traditional FLASH memories. Manufacturing of the memory is low cost, without exotic materials, and compatible to deep nanometers CMOS technology. Access time vs. current and memory device dimensions are presented in this paper.

EP09.03.23
Generic 2D Schrödinger-3D Poisson Solver for AlGaN/GaN Nanowire FinFETs
Viswanathan Naveen Kumar and Dragica Vasilevska; Arizona State University, Tempe, Arizona, United States.

AlGaN/GaN heterojunction FETs (HFETs) possess unique properties such as a wide band-gap, high drift velocity and high critical electric field which make them uniquely suitable for high voltage power devices. Unique properties of Gallium nitride (GaN) such as a wide band gap significantly reduces band to band tunneling making it suitable for sub-10 nm transistors. Ballistic transport is also possible in GaN devices because of the high optical phonon energy. Presence of a 2DEG at the AlGaN/GaN hetero-interface contributes to a high sheet charge density, and subsequently high mobility. However, this very presence of polarization-induced charge density leads to poor turn-off characteristics. In the past decade, 2D FETs, such as FinFETs and Gate-all-around (GAA) FETs, have been developed as viable alternatives to traditional planar transistors. Recent works demonstrate such an approach to AlGaN/GaN HFETs as well. Introduction of non-planarity such as a fin has shown to improve off-state characteristics and push the threshold voltage into the positive. Previous works have shown experimentally the dependence of threshold voltage and the electron density on the width of the nanowire channel.

The focus of this work is to develop a generic 2D Schrödinger-3D Poisson solver for GaN Nanowire FETs. A 3D Poisson solver coupled with a 2D Schrödinger solver allows us to accurately map the charge density in the channel. The solver can also help us model the dependence of electron density in 2DEG and sidewalls on geometry of the nanowire channel. The electron wavefunctions generated by the solver is used to compute overlap integrals in the Ensemble Monte Carlo (EMC) algorithm. Three scattering mechanisms: acoustic phonon scattering, polar optical phonon scattering, and piezoelectric scattering are considered to account for the electron phonon interactions in the system. The EMC solver is then used to determine the low field electron mobility and drift velocity in the channel.

EP09.03.24
Observation of Threshold and Resistive Switching Behaviors in Epitaxially Regrown GaN-p-n Diodes by MOCVD
Hong Chen, Jossue Montes, Chen Yang, Jingan Zhou and Yuji Zhao; Arizona State University, Tempe, Arizona, United States.

Resistive random access memory (RRAM) has been extensively investigated due to its great potential in synaptic and neuromorphic computing applications. In the crossbar array of RRAM architecture, threshold switching selector devices are one of the crucial components to cut off the sneak current path of the unselected cells. This work reported the first observation of threshold and resistive switching behaviors in epitaxially regrown vertical GaN p-n diodes by MOCVD. They showed excellent thermal reliability up to 300 °C, which is a significant improvement over traditional oxide-based devices. The device can be integrated with mature III-nitride high electron mobility transistors (HEMTs) technology and facilitate the development of GaN-based integrated circuits, especially for harsh environments.

The eplayers were grown homoepitaxially on bulk n–GaN substrates by MOCVD. The device structure consists of a 0.5 µm n–GaN buffer layer, a 7 µm unintentionally doped (UID) GaN drift layer, 1 µm n–GaN contact layer, 0.3 µm regrown UID-GaN and 1 µm regrown p-GaN after the etching of 1.5-µm-deep trenches in the UID-GaN drift layer and n–GaN contact layer. The regrown layers on top of the n–GaN contact layer were removed to form the top n-contact. The top p-contact was formed on the regrown p-GaN, and the bottom n-contact was on the backside of the substrate. The forming process was completed by soft break down of either lateral p-n diode between the top n– and p-contact or the vertical p-n diode between the top p-contact and bottom n-contact. After the forming process, we observed the threshold switching process in the vertical diodes with a high resistance state (HRS) and a low resistance state (LRS). Reliability study showed that the devices can operate stably up to 1000 cycles at both room temperature and 300 °C, indicating the excellent thermal stability of the threshold switching behaviors.

The I-V characteristics of the devices was analyzed in log-log scale to explain the operation mechanism. At the LRS, the I-V curve was similar to that of a conventional p-n diode. At the HRS, there are two regions, which follow the trap-assisted space charge limited current (SCLC) theory. At low voltage region, it is dominated by the ohmic law where I V; at high voltage region, it is dominated by the Child’s square law with defects where I V. As shown by the TEM study, the regrowth interface was highly disordered with defects. We hypothesized that after the soft breakdown, the regrowth interface layer may behave like a thin insulating layer with trap states which leads to the HRS. It’s reported that these traps can form/rupture a conductive path by trapping/detrapping carriers. From 0 V to the set voltage, the traps at the interface will be filled with carriers to form a conductive path, resulting in the transition from HRS to LRS. Carriers. From the reset voltage to 0 V, the traps will be depleted of carriers to cut off the conductive path, and the devices change from LRS to HRS. We also observed an increase in set voltage with increasing temperature, which can be explained by the enhanced detrapping effect at high temperatures. Furthermore, the memory behavior can also be observed if the voltage is large than the turn-on voltage of the p-n diode. This is analogous to a diode and a RRAM cell connected in series.

In summary, we demonstrated threshold switching and memory behaviors in epitaxially regrown GaN p-n diodes. This physical mechanism was attributed to the forming/rupturing of the conductive path formed by traps through trapping/detrapping carriers at the regrowth interface. The device showed excellent reliability up to 1000 cycles and thermal stability up to 300 °C. In addition, memory behaviors can be observed when the reset voltage was higher than the turn-on voltage. These results open up opportunities for the development of GaN-based memory devices and integrated circuits.

EP09.03.26
Non-Volatile Discrete Memristive and Memcapacitive States Enabled by Electric Field Controlled Charge Disproportionate Redox
Shreeosh Goswami and Thirumalai V. Venkatesan; NUSNNI, National University of Singapore, Singapore, Singapore.

Handling ‘big data’ is one of the biggest problems for next-generation computing. This calls for major breakthroughs in digital electronics, the backbone of modern computing, where emerging technologies like artificial intelligence is being implemented. For this, memristors are considered an important building block since they facilitate key strategies for big data handling, viz. (i) increasing data density and (ii) reducing the asymptotically increasing demand for computing power. The main challenge in increasing data density is that the existing non-volatile memristors consist of many analog states, suitable for neuromorphic computing but not optimized for a digital platform. We report here a memristor, based on a molecular film of a Ru-complex of an azo-aromatic ligand, having 3 discrete, non-volatile states with conductance values separated by >3 orders of magnitude that are temporally and thermally stable – an ideal candidate for high-density digital electronics. Formation of these discrete states is enabled by field-driven transitions between three different molecular redox states in the film resulting in significant changes in conductance. Of these redox states, the ground state of the film is characterised by charge disproportionation (CD), formation and disruption of which can be reversibly controlled by an external bias at room temperature. Based on electrical and spectroscopic measurements and quantum mechanical calculations, we conclude that the applied field displaces the counterions w.r.t. the molecules, making or breaking the coulombic symmetry and stabilizing the CD and non-CD states. The resulting CD results in a binary memcapacitance concurrent with the ternary memristance and could lead to ultra-low energy computing. In contrast to the highly correlated electronic systems, where only specific physical conditions (like high or low temperature or ultra-high pressure) can cause a broken electronic symmetry (i.e. CD), in our molecular films electronic symmetry/asymmetry (i.e. non-CD and CD states) can be reversibly controlled by external voltage at ambient conditions – one of the Holy Grails in condensed matter physics.

EP09.03.27
Self-Purification of the Highly Pure Semiconducting Carbon Nanotube Arrays
Zhenxing Zhu1, Nan Wei2, Weijun Cheng2 and Fei Wei1; 1Department of Chemical Engineering, Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Beijing, China; 2Department of Applied Physics and Center for New Materials, School of Science, Aalto University, Aalto, Finland; 1Institute of Microelectronics, Tsinghua University, Beijing, China.
Performance Degradation Due to Nonlocal Heating Effects in Resistive ReRAM Memory Arrays

Marius K. Orlovsky and Mohammad Al-Mamun; Virginia Tech, Blacksburg, Virginia, United States.

Conventionally, resistive RAM memory is manufactured in a cross-point architecture. A cross-point at which a memory cell is located, is an intersection of vertical and lateral metal lines for the active and inert electrodes of the resistive memory cell. Here, we investigate the thermally induced degradation of Cu/TaOx/Pt/Ti ReRAM devices. When one cell is repeatedly switched on and off, a certain amount of heat is being deposited in the cell. The local temperature to rupture a Cu filament has been estimated to be 600-800°C. The local heating affects not only the device itself, but the heat dissipated along the electrode metal lines causes performance degradation of the neighboring cells. To monitor the cell degradation we choose specific set condition to form a marginal, i.e. weak, highly resistive Cu filament by imposing low IO of 10μA and ramp rate r=1.2V/s, while the reset is performed at low r=0.1V/s with no IR in order to maximize the Joules heating. Such a fragile Cu filament acts as a canary in the coal mine with respect to ambient heat. The heat deposited in a stressed device leads to a limited number of switching cycles, usually 11-14. When the device is preheated, the maximum number of cycles may decrease to zero and thus as a service for a measure for performance degradation of the neighboring cell. Within 3-4 minutes, after reaching maximal cycles for a given device, we test the switching behavior of the neighboring cells, one at a time. We find that only the cells that share either metal line of the heated device, suffer performance degradation. Direct neighbors (like a cell at the intersection of the adjacent Cu and Pt line) to the heated cell thus not sharing any the electrode of the heated device, are not affected at all by the heat, provided that the intermediate cells are in off-state. However, when the intermediate cells are programmed to the on-state and provide thus a direct heat conduction path to the heated device via copper line, Cu filament of the intermediate cell, and the Pt line, the diagonal neighbors suffers performance degradation. We find that the neighbors along the common Cu electrode line are affected more than the neighboring cells along the Pt electrode line. The heat transport along the Cu line is more effective and reaches further neighbors than for Pt line. Although the heat conductivity of Cu is roughly 3 higher than of Pt and the Cu metal line is 150 nm while the Pt line is 50 nm thick, we found this result surprising because it challenges the conventional assumption that the shape of the Cu filament is that of a sharply tipped cone with a broad base forming an interface with the Pt line and the tip of the cone touching the Cu line. This shape would imply very small contact of the filament with Cu and large contact with Pt, favoring heat transfer to the Pt line rather than to the Cu line. The observed more efficient heat transfer from the filament to Cu than to Pt line implies that the shape of the Cu filament appears to be more likely that of hour glass rather than a cone. When the tested neighboring cells are allowed to cool off for sufficiently long time (20 min or more) they return to the original performance levels of 11-14 cycles. We find also that the minimum cooling off period for cells disposed along the Cu lines rather than along the Pt lines. The width of Cu and Pt lines in our arrays varies between 5 μm and 35 μm and the distance between the lines is ca 150 μm. We find more pronounced degradation of the neighboring cells along the Pt lines, for 35 μm wide Pt lines than for 5 μm wide Pt lines, indicating that metal lines with smaller cross-section are less effective in heat dissipation to the surroundings. In commercial arrays, the thickness, width, and line pitch of the electrode metal lines are of the order of couple 10s of nm. We therefore expect much more pronounced heat effects and over a longer time period in commercial memory arrays.

EP09.03.28

Suppression of Gate-Induced Drain Leakage in Single-Gate Feedback Field Effect Transistors

Dooyeok Lim and Sangsik Kim; Korea University, Seoul, Korea (the Republic of).

In this work, we demonstrate single-gate feedback field-effect transistors (FBFETs) consisting of p'-n-i-n' silicon nanowires (SiNWs). SiNWs were derived from a bulk-Si wafer including ion implantation and crystallographic wet etching processes, and the SiNWs were then transferred onto a plastic substrate. The SiNWs had a diameter of 100 nm, BF2+ and As+ ions were implanted for the formation of p' and n' regions in the p'-n-i-n' SiNWs, respectively. The aluminum electrodes were formed on top of the SiNW in p'-drain and n'-source regions. The i-regions of the channels were covered with Al2O3 high-k dielectric layers. Tungsten top-gate electrodes with widths of 2 μm were also formed via photolithography and thermal evaporation processes. The SiNW FBFET exhibits good switching characteristics in terms of an on/off current ratio, a subthreshold swing, and gate-induced drain leakage (GIDL) current. Specifically, the GIDL can be effectively suppressed because the p' potential barrier in p'-n'-i-n' silicon nanowires can block the injection of tunneling electrons, unlike the conventional metal oxide semiconductor FETs (MOSFETs).

EP09.03.30

Introducing a Single MOF Crystal into a Micro CBRAM Device by a Selective Growth Method of MOF

Atsushi Shimizu1, Kentaro Kinoshita1, Yusuke Nakaume1, Hissashi Shima2, Makoto Takahashi2, Yasuhisa Naioh2 and Hiro Akinaga2; Department of Applied Physics, Faculty of Science, Tokyo University of Science, Katsushika-ku, Japan; 3Emerging Device Group, Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Conducting-bridge resistive random access memory (CBRAM) is attracting attention thanks to its advantages such as low power consumption and high applicability to multi-bit data storage. However, CBRAM has issues to be solved, such as, ex., large deviation of switching voltage and resistance, for putting it into practical use. Above all, semiconductor technology is facing a miniaturization limit that prevents the density of memory devices higher. Metal organic frameworks inherently have periodically and densely aligned subnanoscale subunits that self-assembled to the MOFs. We propose replacing a metal oxide film in a CBRAM cell that works as a memory layer with MOF. This is because we expect the subnanoscale pores of MOF enhance ion diffusion and the directionality of the diffusion along the pores, leading to superior performance including the improvement of the deviations of a switching voltage and resistance. In this paper, to introduce MOF into actual CBRAM devices, we established a method to grow a single MOF crystal selectively at a via. We also show resistive switching behavior observed in the MOF-CBRAM. SiO2 was deposited on a Cu (50 nm)/Pt (20 nm)/TiN (20 nm)/SiO2/ Si substrate, followed by the formation of vias with the diameter of 100 nm, through which the surface of the Cu layer was exposed to the solution, using electron beam lithography. 1,3,5-Benzenetricarboxylic acid (BTC) of 1.8 g was dissolved into the mixed solution of ethanol of 15 ml and dimethylformamide (DMF) of 15 ml. The processed substrate was soaked into the solution to synthesize HKUST-1 [1] that is one of the most popular MOF due to its high stability in the atmosphere. Finally, we fabricated top electrodes of Au (20 nm)/Ti (20 nm), filling the vias, by EB evaporation. Electric characteristics were measured using a semiconductor parameter analyzer (B1500A, Keysight).

In our proposed method, HKUST-1 synthesis advances by dissolving Cu from the Cu layer of the processed substrate into the solution through the vias. Since no Cu is contained in the synthesized MOF, HKUST-1 can be synthesized without the presence of Cu ions. To keep the concentration of dissolved Cu around the via high, another substrate was placed facing the processed substrate through thin glass sheets that works as a spacer. In fact, we confirmed by SEM that a single HKUST-1 crystal was selectively synthesized at the via region. For electric characteristics, our MOF-CBRAM showed relatively low resistance in an initial state. This may be attributed to the presence of residual Cu ions that were not incorporated into the crystal and were left in the pores. Accordingly, electrical preparation process similar to reset, which is resistive switching from a low to high resistance state, is necessary for the development of resistive switching phenomena. After the preparation process, bi-polar resistive switching, which means that bias voltages with different bias polarities are necessary to cause set and reset switching, respectively, was confirmed. Therefore, resistive switching phenomena in a single MOF crystal was achieved as a microfabricated device, for the first time.

In conclusion, we newly developed a method that enables a selective synthesis of MOF crystal accurately at desired points. Combining this method with conventional microfabrication technic that is familiar with silicon process, micro CBRAM cells containing a single MOF crystal each as a memory layer could be fabricated successfully. In addition, our result strongly indicates MOF crystal can be introduced widely into CMOS process.


EP09.03.31

Functional Demonstration of In-Memory Arithmetic Logic Unit in Memristive Crossbar for Software-Defined Memprocessor

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Abstract: Software-defined microprocessor in computing systems provides the convenience for users to execute the wanted functions in intelligent terminals. In the

Carbon nanotubes (CNTs) are the promising candidates for the novel integrated electronics. Whereas, it’s a challenge to obtain perfect semiconducting CNT (s-CNT) arrays with a high purity. Here, we demonstrate the self-organized 99.9999% s-CNT arrays based on an interlocking between the atomic assembly rate and bandgap of CNTs. Rate analysis verified the Schulz-Flory (SF) distribution for both metallic (m-) and s-CNTs, indicating their different decay rates as length increased. Furthermore, s-CNTs exhibited an averaged ten-fold slower decay rate than that of m-CNTs ensuring that the purification of 99.9999% s-CNTs with the diameters centered at 2.40 nm when the length exceeded 154 nm. Transistors fabricated on them delivered a high current of 1.4 mA/μm with an on/off ratio around 1014 and mobility over 4000 cm2/Vs. Our self-purification strategy offers more degrees of freedom to in-situ control the s-CNT purity, exhibiting significant potential in scale-up production and applications of highly pure s-CNTs.
microprocessor, arithmetic logic unit (ALU) with the information processing ability is the kernel. In this work, the in-memory ALU functions are demonstrated in the memristive crossbar with implementing nonvolatile Boolean logic functions and arithmetic computing. For logic implementation, stateful IMP, OR and NOR logic are reconfigured within three devices in one step. Based on them, other logic functions are constructed within five devices in five steps at most. The program voltage amplitude is decreased at a relatively low standard under “≤Vth” mode. For arithmetic computing, the fundamental functions including n-bit full adder with high parallelism, efficient increment, decrement and shift operations are designed and demonstrated for building other arithmetic blocks, such as subtraction, multiplication and division. Furthermore, the energy consumption is estimated and the design of the peripheral circuit is discussed to evaluate the practicability. This work may pave the way for memristor-based logic and arithmetic computing.

EP09.03.32
CBRAM Based on Single Crystalline Si Thin Films Grown by Solid Phase Epitaxy
Inho Kim, Jong-keuk Park, Beomsic Jung and Gun-hee Kim; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).
Low dimensional defects such as dislocation in single crystal Si serve as fast diffusion path of Ag ions. Recently, efforts have been made to employ dislocations in single crystal based oxide and silicon as reliable Ag filaments in CBRAM (Conductive Bridging Random Access Memory). Conductive Ag filaments are reported to be well confined in one dimensional dislocation facets in nanometer scale and exhibit promising device performances in terms of retention time, endurance, linearity and on/off ratio. However, there has been a rare study of controlling the location of the low dimensional defect formation, which is a key factor to device production. In this study, we performed research to create the low dimensional defects on the active region of the epitaxially grown Si thin films for CBRAM by our proposed approach. The single crystal Si thin films were grown by solid phase epitaxy. We fabricated CBRAM devices by sandwiching the epitaxial Si thin films between the active metal of Ag and highly conductive Si substrate. We investigated the device performance of CBRAM including intentionally controlled defects in the epitaxial Si thin films and discuss the effect of the low dimensional defects on the resistive memory device performances. Furthermore, we performed the feasibility study on the use of the epitaxial Si based CBRAM for artificial synapse for neuromorphic computing. The fundamental process parameters of the epitaxial Si CBRAM were extracted, and we propose the future research direction to optimize the device parameters for the artificial synaptic device applications.

EP09.03.33
Nanoscale Electronics Realization with a Prospectives from Devices Architecture and Interconnect Circuits Theory
Preetisudha Meher; National Institute of Technology, Yupita, India.
Nanoelectronics is a natural consequence of the earlier successes of microelectronics. However, this realization is likely to continue provided, all new elements fetched by nanometer era of technologies [P. Meher, et al. IEEE Microelectronics and Electronics, 2012, 229]. The primary interest of this investigation is to raise the level of awareness of the IC design community [P. Meher, et al. Journal of The Institution of Engineers (India)], 96 (2015) 391] that design for cost minimization is likely to emerge as a high priority action item on IC design plans [P. Meher, et al. International Journal of Circuit Theory and Applications, 2018]. Few basic important parameters have been formulated for cost minimization via cost objective function and performance via design density (very large scale integration) and yield concurrently. This understanding helps us to realize the CMOS logic gate with simple model developments for delay and power dissipation estimation [S. R. Ghimiray, et al. International Journal of Circuit Theory and Applications, Wiley, 46 (2018) 1953]. These analysis permit us to understand the mechanisms that control the performance, particularly the power dissipation, of a logic circuit [IEEE Region 10 Annual International Conference, Proceedings/TENCON, 2017]. Several CMOS design styles are attempted with a circuit variations of the static complementary CMOS, which are suitable for low-power applications [S. R. Ghimiray, et al. IOP Conference Series: Materials Science and Engineering- Institute of Physics, 2017].

SESSION EP09.04: RRAM
Session Chair: Peide Ye
Wednesday Morning, April 24, 2019
PCC North, 200 Level, Room 224 B

8:00 AM EP09.04.01
Current Density and Electric Field Decomposition During Nonlinear Electronic Instabilities
Sahas Kumar and R. Stanley Williams; HP Labs, Palo Alto, California, United States.
What physical quantities determine behavior of multistable electronic devices and circuits, especially when multiple stable configurations exhibit identical current, voltage, power input and heat output? This question has been discussed in different forms over several decades. For instance, in 1963 Ridley postulated that under certain bias conditions circuit elements exhibiting a current- or voltage-controlled negative differential resistance will separate into coexisting domains with different current densities or electric fields, respectively. Landauer then postulated that all circuit theorems are in essence heat-generation theorems. These debates were never resolved because of the lack of analytical and experimental techniques to resolve the underlying issues. These issues now assume vital importance especially with the tapering down of Moore's law and the concurrent interest in nonlinear electronic devices such as memristors. We address these issues by using thermal and chemical spectro-microscopy to directly imaged signatures of current-density and electric-field domains in several metal oxides. The local activity theorem successfully predicts initiation and occurrence of spontaneous electronic decomposition, accompanied by a reduction in internal energy, despite identical power input and heat output. This is a process similar to spinodal decomposition of a homogeneous liquid or disproportionation of a metastable chemical compound. This result reveals a thermodynamic constraint required to properly model all nonlinear circuit elements. Our results explain the electroforming process that initiates information storage via resistance switching in metal oxides and has significant implications for improving neuromorphic computing based on nonlinear dynamical devices.
Reference: Kumar and Williams, Nature Communications, 9, 2030 (2018)

8:15 AM EP09.04.02
Bi-Directional Analog Synaptic Behavior of SiOx:Ag-Based Diffusive Memristor
Nasir Ilyas1, Dongyang Li1, Yuhuan Yuan1, Xiadingong Jiang1 and Wei Li1, 2; 1School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China; 2State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China.
Besides conventional digital von Neumann computing system, the brain-inspired neuromorphic system has been proposed as a new computing paradigm considering effective information processing and memorizing simultaneously. Artificial electronic synapses mimicking biological synaptic functions are required for the realization of highly efficient neuromorphic architectures. Therefore, a two terminal memristor based on electromigration of cations (e.g., Ag+) has attracted considerable interests due to its similar behavior with a bio-synapse (e.g., the flux of Ca++ and Na+) at an ionic level. The memristor working on Ag diffusion dynamics in an ionic conductor matrix (i.e., SiOx:Ny, AgS and biopolymer -i-carrageenan) has successfully emulated the Ca++ and Na+ dynamics of bio-synapse. HfOx- or TaOx-based memristors exhibiting gradual resets are also proposed for the adaptive learning to mimic the bio-synapse inhibition process based on the electromigration of the oxygen ions/vacancies under voltage pulses. It is challenging to implement bi-directional analog resistance modulation, i.e., many memristors possess gradual conductance changes only under 1V polarity and cannot dutifully mimic bio-synaptic functions of potentiation and depression. Moreover, bi-directional analog resistive random-access memory (RRAM) is suitable for running more complex deep neural networks. There is no doubt that innovation in the design of a memristor both in materials and electrodes is one of the efficient way to realize this goal. In a memristor, bi-directional analog resistive switching behavior is crucial to adjust the conductance continuously and to mimic various bio-synaptic functions faithfully. The silver-nanoclusters dispersed silicon oxide thin film is an attractive material to fabricate the RRAM devices. It is well-known that in SiOx:Ag-based RRAM devices, the switching mechanism is closely correlated to the formation/dissolution of Ag filaments under an electrical field. Therefore, developing a method to control the filament formation/dissolution is necessary for performance enhancement. Recently, we have proposed a Pt/SiOx:Ag/Ti/Pt memristor which possesses an excellent bi-directional analog resistive switching behavior. We have observed that the formation of a non-stoichiometric high-k TiOx interfacial layer during device fabrication process presents a good barrier property for Ag diffusion under a relatively high electric field. The device has shown a gradual increase and decrease of conductance under positive and negative pulse trains without setting compliance current (iCL). The results of the bi-directional gradual set/reset are a benefit to obtain a reliable “analog” switching for the corresponding synaptic characteristics.
Moreover, the short- and long-term plasticity, paired-pulse facilitation (PPF) and transition from short-term memory (STM) to long-term memory (LTM) have also been realized.

In our Pt/SiO$_2$/Ag/Ti/Pt memristor architecture, a stack of pure Ti-layer and SiO$_2$/Ag composite film was deposited on Pt bottom electrode using DC sputtering and RF co-sputtering, respectively. Subsequently, by using the lithography process, 100-nm-thick Pt top electrodes of 200 nm in diameter were patterned. XPS, XRD and SEM were used to demonstrate the formation of TiO$_2$ interfacial layer during device fabrication process. The resistance switching characteristics have been determined by modulating the interfacial resistance under 0~±1.5V pulse trains using a digital power source (Keithley 2636B) hooked with a probe system.

In short, we have successfully demonstrated a bi-directional synaptic behavior based on Pt/SiO$_2$/Ag/Ti/Pt memristor and proposed a new way for the design of multi-functional resistive switching devices which are promising for future memory and neuromorphic computing applications.

### References


### Introduction

The physical limitations of Si material are faced, the performance improvement of charge storage memories enabled by conventional scaling rules is noticeably slowing. In the meantime, emerging memories that are theoretically advantageous for device scaling based on resistance changes in oxides and chalcogenides driven by spin orientation, phase change, and atomic filament formation have begun to be implemented for a storage class memory, which is a newly introduced technology in the traditional memory hierarchy. Particularly, by employing a cross-point architecture, the memory is sandwiched by perpendicularly located word line and bit line. This passive array allows the highest memory density at the smallest cell size, but is inherently affected by unwanted sneak-path currents generated from adjacent cells, causing read errors. Therefore, a two-terminal threshold selector (TS) that can prevent the sneak-path current below a threshold voltage ($V_{th}$) and provide a sufficient current instantly above the $V_{th}$ is required for each memory cell (1T-1R) in the cross-point array.

From a material perspective, the TS can be realized using certain transition-metal oxides such as VO$_2$, TiO$_2$, and TiN during different RS periods. This highlights the significance of oxide/metal interfaces in RRAM, even in filament type devices. Finally, we developed a RRAM device with geometric confinement of the oxygen vacancy distribution and nanofilament location. The nanotip based devices show good RS properties including forming-free, stable endurance and retention. This demonstrates a route to CMOS compatible devices and an effective way to control cycle-to-cycle resistance switching in RRAM technology. Our progress in understanding the materials issues and RS mechanism, as well as the development of filament confinement solutions, will certainly facilitate the possible regulation of RS modes and thus further the optimization of RRAM device performances.
Ferroelectric Spiking Neurons for Unsupervised Clustering

It is observed that the programming current in a memristor is decreased by using 2D materials. This is enabled by the brain’s synapses which form a highly complex and efficient interconnection between neurons in the brain. Therefore, a nano-electronic device which can emulate brain’s synaptic behavior is needed to enable high accuracy in unsupervised learning, increases sparsity in spiking, and efficient implementation of synaptic weights. Two of the most critical aspects of such a device are 1) the switching medium, and 2) the switching behavior.

In this talk, we will present experimental demonstration of ferroelectric spiking neuron based on a compact 1T-1FEFET structure and compare them to other state-of-the-art memristor devices. These devices are fabricated using a high-yield CMOS process and do not scale down with the scaling of the technology node. Deep neural network (DNN) is a class of artificial neural networks (ANNs) that benefits from both the availability of big data (large amount of multi-media data for model training) and the continual performance improvement of semiconductor technologies in the past decade. However, the memory hierarchy of today’s computing architectures is not specifically designed to leverage the predictable dataflow and potential data reuse of DNN processing, resulting in longer latency and insufficient energy-efficiency for memory access. To reduce these expensive memory access, hardware accelerators for DNNs are designed to employ more fine-grained local memory hierarchy and more specialized dataflow design, which improves the energy efficiency and throughput while maintaining DNN’s inference accuracy. However, the “memory bottleneck” in modern DNNs may not be fully addressed by the acceleration architectures alone. Emerging memory technologies have the potential to play an important and unique role. As these technologies can potentially offer up to tera-bytes of on-chip data storage with a wide range of energy-delay optimization opportunities, they may complement SRAM and DRAM for more efficient DNN inference acceleration. A possible application of the emerging non-volatile memory (NVM) devices is to serve as in-memory computing element where multi-level resistance response of an NVM can store the analog synaptic weights of a DNN on-chip. In another in-memory computing scheme, a crossbar array of non-volatile memory devices can perform the multiply-and-accumulate (MAC) operation at a lower energy cost when the input vector is encoded as analog voltage and the weight matrix is encoded as analog resistance (conductance) values stored in the memory devices. The ability of the NVMs like RRAM, PCM, CBAM to change its resistance values gradually as a function of the applied voltage pulse across its electrode is the key to performing analog in-memory MAC operation.

This paper provides an overview of the current state-of-the-art non-volatile memory devices used for neuromorphic hardwares in applications ranging from biology based learning models to conventional machine learning algorithms solved using neural networks. Furthermore, a more focused overview of the device-level trade-offs required for hardware acceleration of neural network architectures using analog in-memory MAC operation is presented. In general, larger conductance range, more intermediate states, and higher resistance are desirable for both inference and training. For inference, an ideal device should also have linear I-V relationship and long retention time. For training, symmetric and linear pulse response, small device-to-device and cycle-to-cycle variation, and good endurance are crucial.

Our review reveals that controlling the oxygen ion movement during pulsed switching in RRAM can be a promising way to achieve the aforementioned performance goals. Placing an oxygen ion barrier to make a bilayer RRAM and confinement of the generated heat during switching have shown significant improvement in analog switching. Better thermal management in RRAM can also provide filament stability that could improve reliability like retention and endurance. If the ideal device can be achieved, the MAC array using NVMs can provide ultra-low energy, high throughput computing without compromising bit precision that is currently missing in the neural network accelerator landscape.

In this work, we use MoS\(_2\) as the switching medium to fabricate a memristive device. MoS\(_2\) is grown on monolayer graphene forming a vertical heterojunction by the sulfurization of Mo film. Graphene (Gr) is used as the bottom electrode while Ni/Au contact on MoS\(_2\) is the top electrode. The MoS\(_2\)/Gr memristors exhibit memory forming-free non-volatile switching behaviour with a low programming current of 1 nA. In addition, these devices exhibit sub-nW reset power and low energy consumption of ~2 pJ/pulse event which makes them highly energy-efficient. Synaptic characteristics such as multiple conductance states between 1 nA and 1 \(\mu\)A with a minimum reset current of 16 pA is also observed. Furthermore, the MoS\(_2\)/Gr memristors exhibit excellent data retention characteristic of 10\(^5\) s at multiple conductance states viz., 1 nA and 1 \(\mu\)A. Also, MoS\(_2\)/Gr memristors exhibit biological synaptic characteristics like plasticity, multi-state conductance tuning, short and long-term potentiation, long term depression and spike timing plasticity. Additionally, sustained switching at 1 nA and 100 nA programming currents is observed in these devices for 100 DC cycles indicating their robustness.

Filamentary switching with low programmingreset power observed in these devices unravel the prospects of developing nano-scale crossbar arrays of energy-efficient synaptic devices for artificial neural networks.

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6. EP09.05.02/EP08.06.02
7. 10:45 AM
8. EP09.05.03/EP08.06.02
9. Emulating Biological Synaptic Behavior for Ultra-Low Power Neuromorphic Applications Using MoS\(_2\)/Graphene Heterojunctions Adithi Pandapally Krishnamoornad Sharanad 1, Nitin Choudhary, Sonali Das 1, Durjoy Das 1, Hirokjyothi Kalita 2, Hee-Suk Chung 3, YeonWoong Jung 4 and Tanja Roy 1, 2, 3 aNanoScience Technology Center, University of Central Florida, Orlando, Florida, United States; 2Department of Electrical Engineering, University of Central Florida, Orlando, Florida, United States; 3Analytical Research Division, Korea Basic Science Institute, Jeonju, Korea (the Republic of); 4Department of Material Sciences and Engineering, University of Central Florida, Orlando, Florida, United States.
10. The conventional computing systems based on the von Neumann architecture have reached limits in terms of computational power and data dissipation due to increasing computational complexity. To circumvent these issues, new computational architectures are explored, among which neuromorphic computing based on emulating the human brain stands out. It is known that the human brain supercedes a supercomputer by 6-9 orders of magnitude in power dissipation. The superior features of the brain, such as ultra-high density, low-energy consumption, parallelism, robustness, plasticity, and fault-tolerant operation need to be emulated by computing systems for perception and learning. These qualities are enabled by the brain’s synapses which form a highly complex and efficient interconnection between neurons in the brain. Therefore, a nano-electronic device which emulates the synaptic properties is a crucial building block for brain-inspired computational systems.
11. It is observed that controlling the oxygen ion movement during pulsed switching in RRAM can be a promising way to achieve the aforementioned performance goals. Placing an oxygen ion barrier to make a bilayer RRAM and confinement of the generated heat during switching have shown significant improvement in analog switching. Better thermal management in RRAM can also provide filament stability that could improve reliability like retention and endurance. If the ideal device can be achieved, the MAC array using NVMs can provide ultra-low energy, high throughput computing without compromising bit precision that is currently missing in the neural network accelerator landscape.
12. These ferroelectric devices are fabricated using a high-yield CMOS process and do not scale down with the scaling of the technology node. Deep neural network (DNN) is a class of artificial neural networks (ANNs) that benefits from both the availability of big data (large amount of multi-media data for model training) and the continual performance improvement of semiconductor technologies in the past decade. However, the memory hierarchy of today’s computing architectures is not specifically designed to leverage the predictable dataflow and potential data reuse of DNN processing, resulting in longer latency and insufficient energy-efficiency for memory access. To reduce these expensive memory access, hardware accelerators for DNNs are designed to employ more fine-grained local memory hierarchy and more specialized dataflow design, which improves the energy efficiency and throughput while maintaining DNN’s inference accuracy. However, the “memory bottleneck” in modern DNNs may not be fully addressed by the acceleration architectures alone. Emerging memory technologies have the potential to play an important and unique role. As these technologies can potentially offer up to tera-bytes of on-chip data storage with a wide range of energy-delay optimization opportunities, they may complement SRAM and DRAM for more efficient DNN inference acceleration. A possible application of the emerging non-volatile memory (NVM) devices is to serve as in-memory computing element where multi-level resistance response of an NVM can store the analog synaptic weights of a DNN on-chip. In another in-memory computing scheme, a crossbar array of non-volatile memory devices can perform the multiply-and-accumulate (MAC) operation at a lower energy cost when the input vector is encoded as analog voltage and the weight matrix is encoded as analog resistance (conductance) values stored in the memory devices. The ability of the NVMs like RRAM, PCM, CBAM to change its resistance values gradually as a function of the applied voltage pulse across its electrode is the key to performing analog in-memory MAC operation.
13. This paper provides an overview of the current state-of-the-art non-volatile memory devices used for neuromorphic hardwares in applications ranging from biology based learning models to conventional machine learning algorithms solved using neural networks. Furthermore, a more focused overview of the device-level trade-offs required for hardware acceleration of neural network architectures using analog in-memory MAC operation is presented. In general, larger conductance range, more intermediate states, and higher resistance are desirable for both inference and training. For inference, an ideal device should also have linear I-V relationship and long retention time. For training, symmetric and linear pulse response, small device-to-device and cycle-to-cycle variation, and good endurance are crucial.
14. Our review reveals that controlling the oxygen ion movement during pulsed switching in RRAM can be a promising way to achieve the aforementioned performance goals. Placing an oxygen ion barrier to make a bilayer RRAM and confinement of the generated heat during switching have shown significant improvement in analog switching. Better thermal management in RRAM can also provide filament stability that could improve reliability like retention and endurance. If the ideal device can be achieved, the MAC array using NVMs can provide ultra-low energy, high throughput computing without compromising bit precision that is currently missing in the neural network accelerator landscape.
Parallel Programming of an Ionic Floating-Gate Memory Array for Scalable Neuromorphic Computing

**Correlation Between Traps Jumping Distance and Gradual Conductance Change Under Different Conductance Update Schemes in HfOx-based Memristive Devices**

**Memristive Behavior in Core-Shell Nanowire Networks for Neuromorphic Architectures**

**Ultrafast Power Dual Gated Sub-Threshold Oxide Neuristors—An Enabler for Higher Order Neuronal Temporal Correlations**
global neuromodulations, allowing additional modulations which augment their plasticity and enabling higher order temporal correlations at a unitary level. Moreover, the dual-gate operation extends the available dynamic range of synaptic conductance while maintaining symmetry in the weight-update operation, expanding the number of accessible memory states. Finally, operating neuromorphic circuits in the sub-threshold regime enables synaptic weight changes with high gain, while maintaining ultralow power consumption of the order of femto-Joules.

SESSION EP09.06: MoS2
Session Chair: Won Jong Yoo
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 224 B

1:30 PM *EP09.06.01
Excitons in Two-Dimensional Semiconductors “Talking” to Their Environment
Kvirk L. Bolotin; Freie Universitaet Berlin, Berlin, Germany.

Every atom in two-dimensional semiconductors from the group of Transition Metal Dichalcogenides (TMDs) belongs to the surface. Because of that, TMDs are strongly affected by their microenvironment. In this talk we show that excitons, bound electron/hole pairs, in TMDs can serve as exquisite probes of the physical and chemical properties of that microenvironment.

First, we show that TMD excitons are strongly screened by nearby dielectrics. In suspended TMD, the behavior of pristine material is approached. We also examine frequency-dependent screening of excitons in TMD and show that the frequency-dependent dielectric function of the environment can be effectively “sampled” by examining spectral shifts and intensity redistribution between neutral, charged, and defect-bound excitons. Second, we examine near-field energy transfer between TMDs and nanoscale quantum emitters (semiconductor quantum dots or dye molecules) near it. We show that such energy transfer is very efficient, and that its rate can be controlled through electrical gating. Finally, we examine binding of excitons in TMDs to charged molecules on their surface. We demonstrate new molecule-specific excitonic species produced by such binding.

2:00 PM EP09.06.02
Near-Ideal 2D/2D and 2D/High-K Dielectric Interfaces Extracted Using the Conductance Method
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Two-dimensional transition metal dichalcogenides (TMDs) are expected to have significant contributions to the future electronic and optoelectronic devices due to their unique features, such as sizable bandgaps, uniform thickness, absence of dangling bonds, lower trap density, reduced short channel effects, etc. Molybdenum disulfide (MoS2) one well-known TMD, has drawn interest for high speed, flexible, low power electronic devices since it has a tunable bandgap, reasonable carrier mobility, excellent strength and large surface to volume ratio. One of the key reasons for dominance of silicon over all other semiconductors is the high quality interface between Si and SiO2. Any semiconductor system should possess an interface comparable in quality with the Si/SiO2 interface for its reliable application in electronic and optoelectronic devices.

In this work, we studied the interface quality of 2D/2D and 2D/3D interfaces by developing MoS2 based field effect transistors (FET) having hexagonal boron nitride (h-BN) and high-k top gate dielectrics (AlOx and ZrO2). For the 2D/2D MoS2/h-BN FET, 13 nm h-BN flake was dry transferred over exfoliated MoS2. For the MoS2/high k gate dielectric structure, two different nucleation layers SiO2 and AlOx were e-beam evaporated over exfoliated MoS2 prior to atomic layer deposition of high k gate dielectrics AlOx and ZrO2. One of the most direct, precise and sensitive techniques called the conductance method is adopted for extraction of the interface trap density (Dit) [1]. The subthreshold swing for the devices are in the range of 95 mV/decade to 160 mV/decade. In this comparative study, transistors with the MoS2/h-BN 2D/2D interface exhibited lowest trap density in the range of 7×1014 states/cm2-eV at midgap. This superior quality interface is attributed to the absence of dangling bonds at 2D/2D interface [2]. The interface between MoS2 and AlOx exhibited lower trap densities compared to MoS2/ZrO2 interfaces. In the mid gap, the highest trap density (1.35×1015 states/cm2-eV) is obtained for ZrO2 gate dielectric with AlOx nucleation layer, while the lowest one (7×1014 states/cm2-eV near valence band) is obtained for AlO2 gate dielectric with SiO2 nucleation layer. For both AlOx and ZrO2 gate dielectrics, the SiO2 nucleation layer offered lower Dit compared to the AlOx nucleation layer. The interface trap densities obtained by the conductance method are compared with the numbers obtained using other Dk extraction techniques, such as the Terman method and high-low frequency methods. This study shows that the MoS2/h-BN and MoS2/SiO2/AlOx interfaces are at par with the state-of-the-art Si/high-k interface, extending the promise of 2D materials for future high-performance electronics.

References:

2:15 PM EP09.06.03
Effect of Dose Rate on Interstitial-Vacancy Recombination in Silicon During Helium Implantation
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One outstanding issue for state-of-the-art silicon devices is achieving high levels of dopant activation for shallow junctions, particularly for 3D device architectures in which processes like solid-phase epitaxial regrowth cannot be easily integrated. Helium ion implantation offers an intriguing potential method of vacancy engineering that is made possible by the stabilizing effect of helium on vacancy clusters, as well as the ability to subsequently desorb the implanted helium upon low-temperature annealing. However, much is still unknown about the dynamic interactions between helium, vacancies, and self-interstitials in silicon during implantation. In this study, these interactions were investigated by systematically varying the dose rate of an elevated temperature helium implant. 10 keV He+ was implanted into (100) Si at a dose of 4×1014 cm–2 and an implant temperature of 450°C. Beam currents were varied from 2.6 to 10.4 mA. Transmission electron microscopy studies show that extended defects are present in the as-implanted state, and the density of these defects decreases with decreasing dose rate, which is unusual for non-amorphizing implants. In addition, cavities are present and their size and density vary systematically with dose rate as well. Thermal helium desorption spectrometry reveals differences in helium retention. These results are compared to those of silicon self-implantation performed under similar conditions. Implantation damage from silicon does not show the same dose rate effect, indicating the unique role of helium in self-annealing of implantation damage and suggesting that helium-vacancy interactions prevent some fraction of self-interstitials and vacancies from recombining. This study is an important step toward understanding the atomic processes that control the creation of excess vacancies in silicon through helium implantation.

2:30 PM BREAK

SESSION EP09.07: RRAM Materials
Session Chairs: Catherine Dubourdieu and Gang Niu
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 224 B

3:30 PM EP09.07.01...
New Generation of ReRAM Based on Oxidized Carbon Nanofibers  

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This contribution deals with the first time fabrication of graphitic based memories using oxidized carbon nanofibers (ox-CNFs). In our case we what we have obtained are Metal-Insulator-Metal (MIM) structures where the ox-CNFs are the layer sandwiched between two metal contacts. Thanks to that we are able to fabricate Resistance Random Access Memories (ReRAMs) where the resistance of the layer sandwiched changes in a non-volatile way as a function of the bias applied. Indeed thanks to spray-gun deposition method we are able to deposit thin layer of ox-CNFS on 2 metalized inches substrates. The thickness is around 100nm. The bottom contact is based on Pt and the top contacts are achieved using Cu/Al pads. The change of the resistance is related to the alignment of the oxygen vacancies and therefore to the creation of conductive paths inside the ox-CNFS layers. These paths are disaggeregated cycling the bias. Moreover the oxygen is moved to the top contact and therefore this last is oxidized moving from a low resistance state (LRS) to a high resistance state (HRS). This change is reversible. The results show a typical shape of bi-polar memories when the voltage is cycled between -2 and 2 Volts. We fabricated hundreds of structures and 2/3 showed this behavior. The switching phenomenon is not reproducible if we use CNFs with metal impurities. Indeed in this case the voltage is at the origin of the alignment of the metal impurities that lead to the short circuit of the structure linking the two metal contacts (creating sort of dendrites). For this reason the purification of the fibers is a very important step. The results obtained are extremely interesting and promising result considering that this was the first time in the world that this kind of memories were fabricated and tested. Moreover the ox-CNFs are deposited using spray-gun technique where the CNFs are in stable suspensions in deionized water. This is very important in case of the implementation of the process on very large surface of through roll-to-roll fabrication in order to achieve a low-cost but also operator-friendly process suitable for industrial application.

3:45 PM EP09.07.02  

Impacts of an Asymmetric Stack Structure in TaOx-Based ReRAM Cells on Resistive Switching Characteristics  

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Resistive Random Access Memories (ReRAM) have huge possibilities for contributions to emerging nonvolatile memories. ReRAM cells exhibit reversibly transitions between high resistance states (HRS) and low resistance states (LRS), which is called resistive switching (RS) phenomenon. Set and reset processes mean the transition from HRS to LRS and that from LRS to HRS, respectively. RS operations are classified as either unipolar- or bipolar-type based on polarities of applied voltage at set or reset processes. ReRAM cells with an asymmetric stack structure usually exhibit bipolar RS operations based on valence change mechanism (VCM) [1]. However, why the asymmetric structure results in bipolar RS characteristics have not been clarified yet completely. In this work, we investigated impacts of an asymmetric stack structure in TaOx-based ReRAM cells on resistive switching characteristics.

Pt/TaOx/Pt and Pt/TaOx/TaOx/Pt stack structures were fabricated. The oxide layers were deposited on Pt/Ti/SiO2/Si substrates as bottom electrodes (BEs) by reactive radio-frequency sputtering. The oxygen composition x in the TaOx layers was controlled to be less than 2.5 by adjusting the oxygen gas flow rate. Then, the Pt layers with a diameter of 100 μm were deposited by electron beam evaporation as top electrodes (TEs). The resistance of Pt/TaOx (5 nm)/Pt cells at 0.1 V in an initial state was roughly 10^8 Ω. On the other hand, that of Pt/TaOx (10 nm)/TaOx (5 nm)/Pt cells was approximately 10^4 Ω. The reduction of resistance by introducing the TaOx layer indicates that diffusion of oxygen vacancies (Vo) from the TaOx layer to the TaOx layer caused film thickness distribution of Vo in the TaOx layer. Consequently, the TaOx layer was effectively composed of a sub-stoichiometric layer (TaOx-δ) and a stoichiometric layer (TaOx).

When a positive voltage was applied to the TEs in the initial state, transition to a particular HRS occurred. We have reported the transition from the initial state to the particular HRS by overcurrent suppression in Pt/TiOx/Pt cells [2]. The particular HRS is referred to as semi-HRS. In the semi-HRS of Pt/TaOx/TaOx/Pt cells, as a negative bias increased, the resistance decreased discretely once, and then increased continuously to reach similar resistance to the initial state. These phenomena originate from the migration of Vo by drift due to electric field and diffusion due to Joule heating. After the gradual reset, a set process occurred as a positive bias increased. The characteristics observed in the semi-HRS are quite different from those of conventional bipolar RS. Moreover, the transition to the semi-HRS is necessary for the bipolar RS operations in Pt/TaOx/TaOx/Pt cells.

These results suggest that understanding of characteristics observed in the semi-HRS is highly significant for elucidation of bipolar RS operations in VCM-type cells. We will discuss characteristics in the semi-HRS and mechanism of the bipolar RS operations in detail.


4:00 PM EP09.07.03  

Non-Volatile Electrochemical Memory Operating Near the Thermal Voltage Limit  

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Non-volatile, electrically addressable memories like flash, phase-change, and filament forming metal oxides are desirable as synapses for neuromorphic analog computation with the potential to significantly lower power compared to digital processors. Reducing the switching voltage of non-volatile memories is important both to reduce energy consumption and to prevent dielectric breakdowns. Due to the Boltzmann distribution of electrons, it is unclear if any memory can switch significantly below 1V; developing non-volatile memory operating near the thermal voltage limit is a grand challenge.

In this work, we integrate two silicon-free electrochemical devices to demonstrate non-volatile memory that operates as low as 170 mV, just six times the thermal voltage limit. The first device is an ion insertion transistor which electrochemically shuttles lithium ions and electrons between the gate and the channel, analogous to a battery. Because the ions are mobile and move with the electrons, the process is charge neutral, and up to 10^17 cm^-2 of electrons and ions can be reversibly shuttled between the gate and channel without electrostatic charging. The second device is a diffusive memristor operating based on facile Ag²⁺ migration and filament formation only in the ON state. This diffusive memristor ensures that the ion insertion transistor maintains its state when not electrically addressed. The combination of high charge density of the ion insertion transistor and low leakage current of the diffusive memristor enables these two electrochemical devices to retain memory. Because both devices operate at low voltage, we can linearly tune the electronic conductance using sub-200-mV voltage pulses. This device is also compatible with a V/2 crossbar select scheme without a select transistor, and demonstrates that non-volatile synaptic memory near the thermal voltage limit is possible for low-power electronics.

4:15 PM EP09.07.04  

Spatial Distribution of Conductive Filaments and the Effect of Device Geometry  

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Characteristic resistance changes are observed in two-terminal metal-oxide-metal (MOM) structures when subjected to large electric fields or current densities and are of interest as the basis of nonvolatile memory and neuromorphic computing devices. These resistance changes are often mediated by filamentary conduction, either in the form of a semi-permanent filament created by compositional changes in the oxide or as a transient filament created by inhomogeneous current or field distributions (e.g. current bifurcation). Knowledge of the filament location and morphology, and how these are affected by device geometry and material processing is important for understanding device operation and scaling. For example, enhanced filament formation is expected around the edges of cross-point devices due to local field enhancement or variations in oxide thickness. To gain an understanding of such effects it is desirable to have a simple, robust method of detecting and mapping filaments and to use this to study the statistics of filament formation.

To this end we have developed a simple technique for detecting the location of both permanent and transient filaments based on thermal denaturing of a thin photosensitive layer. The efficiency of this approach is demonstrated by applying it to a MOM cross-point structure comprised of a Pt (25 nm)/Cr (10 nm)/NbOx (45 nm)/Pt (25 nm) heterostructure, with cross point areas of 4x400 μm². A thin positive photosenset layer is deposited on top of fabricated cross-point devices by spin coating and then patterned using photolithography to open access to probe pads. The photosensit is then baked for 2 minutes in air using a hot plate kept at a temperature of 85 °C. After electroforming, a dark spot appeared in the photosensit on the top electrode due to local Joule heating, clearly identifying the filament location. Such analysis is subsequently employed to investigate the number and spatial distribution of filaments produced by electroforming.
Forming is an initial stage required to create conductive filaments in binary transition metal oxides (TMOs) before resistive switching (RS). The dissolution and reformation of the filaments have been widely recognized as an origin of the RS operation. However, where the filaments are created by forming remains unclear. In this study, we investigated correlation between the crystallinity and oxygen composition of TMOs and forming characteristics in TMO-based RS cells.

Pt/(NiO)/Pt and Pt/(TiO2)/Pt cells were prepared. Pt bottom electrodes were deposited by sputtering (SP) or electron beam (EB) evaporation, which is referred to as SP-Pt or EB-Pt, respectively. NiO and TiO2 thin films as binary TMOs were deposited by reactive sputtering. Pt top electrodes were deposited on the TMO layers by EB evaporation. In-plane X-ray diffraction and transmission electron microscopy reveal that NiO layers on the SP-Pt or EB-Pt include columns or granules with a grain diameter of tens of nm, respectively. On the other hand, the crystal orientation of TiO2 layers on the SP-Pt is greater than that of TiO2 layers on the EB-Pt even though the grain size of both TiO2 layers is the same. These results indicate that the crystallinity of TiO2 layers strongly depends on the crystallinity of Pt bottom electrodes [1].

Next, characteristics of the initial cell resistance (Rini) were investigated. In both cases of NiO and TiO2, the Rini values on the SP-Pt were greater than those on the EB-Pt, and the variation of Rini on the SP-Pt were much smaller than that on the EB-Pt. These results suggest that the grain boundary density in TMO layers on the SP-Pt is lower than that in TMO layers on the EB-Pt resulting from the difference of TMO crystallinity. Moreover, TMO layers on the SP-Pt contains fewer oxygen vacancies than those on the EB-Pt, as estimated from our previous results of the segregation of oxygen vacancies at grain-boundary triple points in NiO layers [2]. As a result, the oxygen composition of TMO layers on the SP-Pt is larger than that of TMO layers on the EB-Pt.

Finally, the time to forming (tform) in the cells was measured while keeping a constant applied voltage. All of the cells were confirmed to show repeatable RS operations after forming. Although the variation of tform decreased as the variation of Rini decreased in the case of TiO2 layers, the variation of tform increased as the variation of Rini decreased in the case of the NiO layers. The distribution of forming characteristics depends on both crystallinity and oxygen composition of TMO layers because of the different deposition methods of the Pt bottom electrodes. These clear difference might originate from differences in the oxide deposition mode during reactive sputtering.

The emergence of ferroelectricity in doped HfO₂ thin films has attracted a great deal of attention since its discovery in 2011. Their full compatibility with the complementary metal-oxide semiconductor (CMOS) process make them viable candidates for application in non-volatile memory devices. Amongst hafnia based materials, Hf₁₋ₓZrₓO₂ (HZO) has shown to be one of the more promising candidates. The reason for selecting HZO is a wider and hence more forgiving composition window in mixing HfO₂ and ZrO₂ to obtain ferroelectricity, compared to e.g. Si doped HfO₂. The ferroelectricity in thin doped HfO₂ films is generally accepted to originate from the crystallization of a non-centro-symmetric orthorhombic phase with the space group Pca2₁. During the crystallization, the temperature profile needs to be well controlled in order to favor the formation of the metastable ferroelectric orthorhombic phase against other non-ferroelectric phases. Here we report on the utilization of millisecond Flash Lamp Annealing (ms-FLA) for the stabilization of ferroelectric Hf₁₋ₓZrₓO₂ (HZO) films. The thin film characterization structures are of MIM type and consist of a bottom TiN electrode, a 3-10 nm thick HZO layer and a top TiN electrode, deposited by atomic layer deposition in the same order. For the 10 nm thick HZO sample, the combination of a 120 s long preheat step at 375°C with a 20 ms xenon flash lamp pulse results in ferroelectric characteristics comparable to those obtained when using a 300 s long rapid thermal anneal (RTA) at 650°C. This statement is supported by X-ray diffraction, capacitance voltage, polarization hysteresis and cycling measurements. In 10 nm thick HZO layers a remanent polarization (P_r) of ~21 μC/cm² and a coercive field (E_c) of ~1.1 MV/cm are achieved. Cycling analysis shows an increase of endurance for the ms-FLA compared to RTA by one decade, up to 10⁵ bipolar cycles. An additional SiO₂ encapsulation of the TiN/HZO/TiN stack further increases the endurance up to 10⁶ cycles. For the 3 nm thin HZO sample the preheat temperature of the ms-FLA was increased to 550°C to successfully crystallize HZO in the orthorhombic/tetragonal phase. Unlike for standard anneals, the ms-FLA annealed films do not show any parasitic monoclinic phase, as confirmed by X-ray diffraction measurements. This illustrates the benefits of a fast thermal process to stabilize ultra-thin ferroelectric films, which are promising candidates for non-volatile memory and neuromorphic hardware applications when used as tunnel junctions.

HfO₂-ZrO₂ composites and alloys are of growing interest as dielectrics in advanced DRAM capacitors and ferroelectric devices in emerging non-volatile memory and negative-capacitance FET technology. These versatile oxide materials express dramatically different physical properties depending on their crystal structure, which can be selected by tuning film thickness, processing conditions, or substrate material. In thin films or nanostructures, the P₄/nmc tetragonal (t) phase, which is a high-k dielectric material, and the Pca₂ orthorhombic (oFE) phase, which is ferroelectric, can be stabilized relative to the low-energy P₄/m monoclinic (m) phase. Establishing predictive relationships between thin film processing and device performance therefore requires accurate measurement of the crystal phase distribution. While possible crystal phases can be inferred by electrical testing, the structure may be changed by electric field-induced transformation. X-ray diffraction (XRD) is the workhorse method of non-destructive crystal phase analysis, but the t and oFE phases are notoriously difficult to discriminate. However, differences in the short-range order of metastable ferroelectric orthorhombic and non-ferroelectric phases are notoriously difficult to discriminate. However, differences in the short-range order of t(Hf,Zr)O₂ and oFE-(Hf,Zr)O₂ are readily distinguished using extended X-ray absorption fine structure (EXAFS) measurements. Using a novel EXAFS analysis method, we resolve the φ, ω, and m phase fractions to within 10% in 6 nm nanolaminate bilayers grown by atomic layer deposition (ALD). This structural analysis technique could inform device processing workflows that favor either ferroelectric or high-k dielectric ultrathin (Hf,Zr)O₂ films.
Promising technology boosters for future scaled CMOS can be regarded as 3D nano-sheet (NS)/nano-wire (NW) structures, new channel materials and the combination. Thus, MOSFETs with alternative channels such as Ge and III-Vs on the Si platform have been strongly expected over recent 15 years for high performance and low power logic devices, where the reduction in Vth is the most critical requirement. CMOS using these channels can reduce the gate overdrive (Vg-Vth) and resulting low Vth at a given ion, because of the increased injection velocity due to the low effective mass. These high mobility channels can be more important for NS/NW CMOS than FinFETs, because of limited rooms to increase the channel width, different from FinFETs. In spite of the strong efforts to introduce such alternative channels, however, the implementation into the advanced CMOS platform has not been visible yet, because of wide aspects of difficulties in the device integration. In the more-Moore approach, Ge/Ill-V III-2D structures for stacked CMOS is one of the promising device structures. This is because 3D integration by using low temperature process is much easier for Ge and III-V than Si. In addition, the ultralow contact resistance of Ge and InGaAs with metals can be expected through utilizing Fermi-level pinning of the interfaces with meals under low thermal budget. In the beyond-CMOS approach, on the other hand, steep slope devices have stirred a strong interest from the viewpoint of ultralow power applications. One of the most promising steep slope devices is tunneling-FETs (TFETs). Here, Ge/III-V channels are also expected to enhance the TFET performance, because of the increased tunneling probability due to the small direct bandgap. Furthermore, in the source/channel junctions composed of the type-II hetero-structure are quite effective in improving the TFET characteristics, because the effective bandgap (DEG) between the valence band top of the source and the conduction band bottom of the channel is reduced, resulting in the increase in ion with maintaining low Ioff.

In this paper, we briefly address the current status of MOSFETs and TFETs using alternative materials such as Ge, III-V and oxide semiconductors for future low power scaled devices and review the recent progress in device and process technologies on a basis of our research activities. Among these devices, Ge pFETs can be the closest to the real applications. Although InGaAs-based nFETs are also promising, stringent controls of material quality and super-smooth device geometry are strongly needed. Since Ge nFETs and III-V pFETs are still in an immature stage, the combination of InGaAs nFETs and Ge pFETs and, in particular, the combined 3D stacked CMOS seem promising. We presented highly-strained GOI and InGaAs-OI formation technologies and ultra-thin body InGaAs QW channel design as viable solutions for advanced CMOS. Also, the introduction of alternative channels is more essential for improvement of TFET performance. The possibilities of Ge complementary TFETs and InGaAs QW TFETs were addressed. Here, the suppression of defect-related currents is a key issue. Finally, we proposed and demonstrated the novel bi-layer TFETs using the type-II hetero-structures composed of oxide semiconductors such as ZnO and ZnSnO, and column-IV semiconductors such as Si, SiGe and Ge. We have experimentally demonstrated the operation of Si/ZnO and Ge/ZnO TFET operation with remarkably high Ion/Ioff of ~10^8, low Ioff and minimum SS of 71 mV/dec. As a result, the oxide semiconductors/ column-IV semiconductor bi-layer TFETs are expected to be one of the potential options of TFETs overcoming CMOS in terms of the ultra-low power operation.
nucleate and grow into SiO2 precipitates (oxide precipitates, OPs) under certain high temperature treatments. Small OPs can pin dislocations and slow slip propagation. Large OPs, however, can soften the wafers both by consuming the dissolved Oi, reducing dislocation locking, and by acting as dislocation sources. It is well known that oxygen forms thermal donors at low annealing temperature (300 – 450 °C), which can result in deleterious resistivity shift, as the same temperature range is often used for post-metalization annealing. In RF devices, where high resistivity of the substrates is critical, ultra-low oxygen concentration ([Oi]) wafers are widely used to reduce thermal donor generation. Due to the lack of Oi to lock and pin the dislocations, low [Oi] wafers are weaker and more prone to slip and plastic deformation. Nitrogen doping is known to be effective in locking dislocations and can be added to the crystal to increase strength, but in combination with oxygen generates new donors, which are stable at higher temperatures (up to 1000°C), exacerbating resistivity shift issues.

Germanium (Ge) seems to be a good candidate for strengthening Si, as it is electrically neutral and forms a solid solution with Si at all concentrations. Ge may impede dislocation motion directly by means of its larger atomic size compared to Si, or indirectly through changing the behavior of Oi diffusion and/or precipitation. Little data is available on the effect of Ge doping on the dislocation motion in silicon wafers with ultra-low [Oi] (1.5 – 3 × 10^{19} atoms/cm²). Previous work on Ge at high [Oi] (5 – 12 × 10^{17} atoms/cm²) reported improved slip resistance, due to Ge enhancing Oi precipitation to pin the dislocation motion. It is unclear whether Ge, as a substitutional impurity, can diffuse to the dislocation cores to prevent the dislocation motion by locking, or retard slip propagation by solid solution strengthening.

In this work, we study the dislocation unlocking stress of ultra-low [Oi] Si wafers (1.5 – 2 × 10^{17} atoms/cm²) with Ge doping (5 – 6 × 10^{19} atoms/cm²). Samples with similar [Oi] but without Ge were used as control. Both types were annealed for various times (0.25 – 16 hours) and temperatures (600 – 750 °C) before mechanical testing, to allow the impurities to diffuse and bind to the dislocations. The samples were then loaded in a three-point bending configuration, and the stress required to unlock dislocations was evaluated. The pinning effect of OPs was negligible at such low [Oi], where precipitation was suppressed, which allowed us to investigate the role of Ge on dislocation motion. The average dislocation velocities as a function of shear stress were found to be comparable for Ge and control groups, and independent of the annealing condition prior to mechanical loading. At all annealing temperatures tested, the unlocking stress as a function of annealing time initially rises linearly before taking a constant value. The saturated unlocking stress is lower at higher temperature, indicating the impurities have a higher tendency to “boil off” from dislocations. The rate of the initial rise is found to be strongly dependent on annealing temperature, with an activation energy of 1.52 eV and 1.68 eV for Ge doped and control samples, respectively. The preliminary results showed that Ge by itself does not have a significant impact on the dislocation unlocking stress for the annealing conditions tested.

References:
As FinFET scaling continues for advanced CMOS nodes (10/7nm), contact resistance remains a dominant component affecting device performance. The FinFET S/D contact area has become smaller with scaling (narrower fins due to reduced fin pitch), resulting in drastically increased contact resistance. To achieve higher drive currents and fully realize the performance gain from FinFET architectural changes such as narrower and taller fins, it is critical to achieve contact resistivity $\rho_{c} < 1.0 \times 10^{-4}$ $\Omega \cdot \text{cm}^2$ for both PMOS and NMOS. In this paper, we first review the requirements and recent trends for contact resistance reduction for advanced CMOS devices. Then, we discuss the various approaches that have recently demonstrated reduction in $\rho_{c}$, such as the use of in-situ heavily doped epitaxial films for S/D, and advanced implant and anneal techniques. The implant techniques leverage damage engineering concepts and include (i) pre-silicide amorphization, (ii) cryogenic (-100°C) implantation and (iii) plasma doping (PLAD) for conformal doping. With such high levels of doping from epit and implant approaches, this paper will also discuss the integration of advanced laser anneal techniques for improved dopant activation while minimizing diffusion, such as millisecond laser anneal, and nanosecond laser anneal (for super-activation), that are imperative for contact resistance reduction. Finally, we will discuss an alternative contact approach, which implements wrap-around contacts that cover the entire S/D fin surface in order to increase the effective contact area while maintaining the same contact size, potentially providing a pathway to further reduce the contact resistance for advanced CMOS nodes.

In summary, incorporating Ti into GeO$_2$ improved. Therefore, Ti-GeO$_2$ confirms a uniform passivation layer prior to deposition with a roughness of 2.9 Å. After 10 ALD cycles of MoSi$_2$, the number of particles taller than 1 nm are reduced by a factor of 4 compared with unpassivated MoSi$_2$. Nuclei on unpassivated SiO$_2$ are roughly 8 nm in height, corresponding with the expected thickness of MoSi$_2$ deposited on Si, whereas on the passivated sample are ~4-8x shorter, consistent with delayed nucleation due to the protection of SiO$_2$. Atomic layer deposition (ALD) processes for high-aspect ratio pattern exist for both Co and Ru, but the need for longer grains requires highly-selective ALD processes proceeding from the bottom-up. Ideal processes nucleate well only Si or metal surfaces, but surface defects on SiO$_2$ and low-k dielectrics can cause unwanted nucleation. In this work, the effectiveness of a self-assembled organic monolayer as both a diffusion barrier and as a passivation agent to enhance selective ALD is investigated.

Previous studies on alternative diffusion barriers have involved amorphous Co-Ti alloys deposited via RF sputtering. Alternatively, sub-2nm thick SAMs containing bulky groups with N or P atoms have also proven to be effective as Cu diffusion barriers on Si and SiCOH. To enhance selectivity of ALD processes, SAMs composed of hexamethyl-disilazane (HMDS) and octadecyl-trichlorosilane (ODTS) have been used to block hydroxyl sites, preventing deposition of HfO$_2$ on SiO$_2$ without blocking deposition on Si. However, these SAMs require extended treatment periods of 24-48 hours. This work demonstrates the use of the molecule 2-diphenylphosphino-ethyl-triethoxysilane (DPPETS), known to be a Cu diffusion barrier, and in the present work, as a rapidly-acting ALD passivant for middle-of-line and back-end-of-line. X-ray photoelectron spectroscopy (XPS) is used to investigate the chemical state of the passivated and unpassivated dielectric surfaces after ALD. On SiO$_2$, passivation of surface defects is observed, with an increase of contact angle from 40° to 82°. However, on SiCOH, the contact angle is not significantly affected by DPPETS passivation.

As FinFET scaling continues for advanced CMOS nodes (10/7nm), contact resistance remains a dominant component affecting device performance. The FinFET S/D contact area has become smaller with scaling (narrower fins due to reduced fin pitch), resulting in drastically increased contact resistance. To achieve higher drive currents and fully realize the performance gain from FinFET architectural changes such as narrower and taller fins, it is critical to achieve contact resistivity $\rho_{c} < 1.0 \times 10^{-4}$ $\Omega \cdot \text{cm}^2$ for both PMOS and NMOS. In this paper, we first review the requirements and recent trends for contact resistance reduction for advanced CMOS devices. Then, we discuss the various approaches that have recently demonstrated reduction in $\rho_{c}$, such as the use of in-situ heavily doped epitaxial films for S/D, and advanced implant and anneal techniques. The implant techniques leverage damage engineering concepts and include (i) pre-silicide amorphization, (ii) cryogenic (-100°C) implantation and (iii) plasma doping (PLAD) for conformal doping. With such high levels of doping from epit and implant approaches, this paper will also discuss the integration of advanced laser anneal techniques for improved dopant activation while minimizing diffusion, such as millisecond laser anneal, and nanosecond laser anneal (for super-activation), that are imperative for contact resistance reduction. Finally, we will discuss an alternative contact approach, which implements wrap-around contacts that cover the entire S/D fin surface in order to increase the effective contact area while maintaining the same contact size, potentially providing a pathway to further reduce the contact resistance for advanced CMOS nodes.

In summary, incorporating Ti into GeO$_2$ improved. Therefore, Ti-GeO$_2$ confirms a uniform passivation layer prior to deposition with a roughness of 2.9 Å. After 10 ALD cycles of MoSi$_2$, the number of particles taller than 1 nm are reduced by a factor of 4 compared with unpassivated MoSi$_2$. Nuclei on unpassivated SiO$_2$ are roughly 8 nm in height, corresponding with the expected thickness of MoSi$_2$ deposited on Si, whereas on the passivated sample are ~4-8x shorter, consistent with delayed nucleation due to the protection of SiO$_2$. Atomic layer deposition (ALD) processes for high-aspect ratio pattern exist for both Co and Ru, but the need for longer grains requires highly-selective ALD processes proceeding from the bottom-up. Ideal processes nucleate well only Si or metal surfaces, but surface defects on SiO$_2$ and low-k dielectrics can cause unwanted nucleation. In this work, the effectiveness of a self-assembled organic monolayer as both a diffusion barrier and as a passivation agent to enhance selective ALD is investigated.

Previous studies on alternative diffusion barriers have involved amorphous Co-Ti alloys deposited via RF sputtering. Alternatively, sub-2nm thick SAMs containing bulky groups with N or P atoms have also proven to be effective as Cu diffusion barriers on Si and SiCOH. To enhance selectivity of ALD processes, SAMs composed of hexamethyl-disilazane (HMDS) and octadecyl-trichlorosilane (ODTS) have been used to block hydroxyl sites, preventing deposition of HfO$_2$ on SiO$_2$ without blocking deposition on Si. However, these SAMs require extended treatment periods of 24-48 hours. This work demonstrates the use of the molecule 2-diphenylphosphino-ethyl-triethoxysilane (DPPETS), known to be a Cu diffusion barrier, and in the present work, as a rapidly-acting ALD passivant for middle-of-line and back-end-of-line. X-ray photoelectron spectroscopy (XPS) is used to investigate the chemical state of the passivated and unpassivated dielectric surfaces after ALD. On SiO$_2$, passivation of surface defects is observed, with an increase of contact angle from 40° to 82°. However, on SiCOH, the contact angle is not significantly affected by DPPETS passivation.

AFM of the SiO$_2$ after HF pre-clean, after DPETPS passivation at 1 hr, and after 10 cycles of MoSi$_2$ ALD on both passivated and unpassivated SiO$_2$ over a 2x2 µm region confirms a uniform passivation layer prior to deposition with a roughness of 2.9 Å. After 10 ALD cycles of MoSi$_2$ on passivated SiO$_2$, the number of particles taller than 1 nm are reduced by a factor of 4 comparing with unpassivated SiO$_2$. Nuclei on unpassivated SiO$_2$ are roughly 8 nm in height, corresponding with the expected thickness of MoSi$_2$ deposited on Si, whereas on the passivated sample are ~4-8x shorter, consistent with delayed nucleation due to the protection of SiO$_2$ defect sites by the DPETPS monolayer. As shown in XPS studies on Si, deposition readily proceeds as metallic MoSi$_2$, whereas on unpassivated SiO$_2$, only 5.6% residual Mo is present at the surface. However, on DPETPS passivated SiO$_2$, Mo content is reduced to 1.4%. On the unpassivated SiO$_2$, a metallic Mo component is observed, consistent with partial MoSi$_2$ deposition. However, on the passivated SiO$_2$, no metallic Mo component is observed, consistent with nucleation of Mo on -OH sites forming Mo$_2$O$_5$. The Mo present being an oxidized state is consistent with MoO$_3$ nuclei on remaining defect sites blocking further Mo deposition.
References:


3:20 PM EP09.09.04
Area Selective Atomic Layer Deposition of MoSiO2 on Si (001) in Preference to SiO2; Jong Youn Choi1, Christopher Ahles1, Keith Wong2, Srinivas Nenni2, Ellie Yieh2 and Andrew Kummel1; 1University of California, San Diego, La Jolla, California, United States; 2Applied Materials, Inc., Santa Clara, California, United States.

Abstract pending

2:45 PM EP09.09.05
Suppression of the Interfacial Layer and Improvement in Electrical Properties of High-K Gate Stack by Atomic-Layer-Deposited AlN Buffer Layer; Chin I Wang1, Teng Jan Chang1, Chun Yuan Wang1, Yu Tung Yin1, Jing Jong Shuye1, Hsin-Chih Lin1 and Min Jiang Chen1; 1National Taiwan University, Taipei, Taiwan; 2Academia Sinica, Taipei, Taiwan.

For high-performance nanoscale transistors and extension of CMOS roadmap, there are still many difficulties that need to be overcome. A low-grade interfacial layer (IL) between high-K gate dielectrics and semiconductors, which results in current degradation, low gate capacitance, and severe short channel effect, is one of the most important issues. However, it is difficult to prevent the formation of the thermodynamically unstable low-K IL such as SiO2 and GeO2. Hence we come up with a concept of introducing a non-oxygen buffer layer between high-K gate dielectrics and semiconductors. In this study, aluminum nitride (AlN) of good chemical stability and electrical characteristics is used as the buffer layer between the crystalline zirconium oxide (ZrOx) high-K gate dielectric and the semiconductor to restrain the formation of the low-K, unstable IL. A suppression of IL is confirmed by the X-ray photoelectron spectroscopy and the high-resolution transmission electron microscopy. A reduction in the equivalent oxide thickness and the leakage current density (JL) are achieved by the AlN buffer layer. In addition, a decrease of interface trap density (DOI) is accomplished because of the hydrogen passivation from the remote hydrogen plasma during the AlN deposition. All the results indicate that the AlN buffer layer is effective in providing a high-quality interface to improve the performance of advanced metal-oxide-semiconductor field-effect-transistors.

3:00 PM BREAK

3:30 PM EP09.09.06
High Reliable High-K Dielectric Oxide-Based Nanolaminates for Next Generation Logic Analog and Memory Semiconductor Devices; Yuanning Chen1, Chun Wu2, Deborah Riley1, Israel Mejia1, Jesus Alcantar2 and Orlando Aucillio1; 1MicroSol Technologies Inc., Dallas, Texas, United States; 2The University of Texas at Dallas, Richardson, Texas, United States.

A novel structured material in thin film form, Sub-Nanometer Periodic Stack Dielectrics (SN-PSD) has been developed for applications to a new generation of logic analog and memory semiconductor micro/nano-devices. Compared with conventional single layer dielectric films, SN-PSD exhibits substantial improvement in dielectric breakdown voltage (~2.4V, or 35% improvement), and reduced leakage current by about one order of magnitude. High-density capacitor structures utilizing SN-PSD layer would enable on-chip decoupling capacitors in digital and analog integrated circuits (ICs), data storage elements in IR image sensors, energy storage in transmitters, and DRAM and other semiconductor memories to improve the performance and reduce the silicon footprint. The SN-PSD would also be suitable for use as a gate dielectric in silicon carbide (SiC) CMOS FETs for its low leakage current and high breakdown voltage. Existing single-layer-dielectric capacitors often have a large footprint, and have issues with high leakage current and early dielectric breakdown, making their use in developing devices problematic. The time-dependent dielectric breakdown lifetime extrapolation for SN-PSD indicates that the dielectric breakdown lifetime will exceed 10 years under equivalent electric field of 15.6MV/cm for HfO2/TiO2 SN-PSD-based capacitors, versus 9.1MV/cm for single layer HfO2-based capacitors. Compared to single layer HfO2 capacitors, the breakdown mechanism of the newly developed HfO2/TiO2 SN-PSD capacitors has been changed from hard breakdown to soft breakdown. The capacitance voltage (C-V) characteristics have been analyzed. The charge and discharge cycle has been studied for 10,000 cycles without degradation. The frequency response of capacitor has been characterized for frequencies of 10Hz, 100KHz, and 1MHz. Underlying mechanisms for the SN-PSD functionalities will be discussed.

3:45 PM EP09.09.07
Vertical GaN p-n Diode with Regrown p-GaN by Metalorganic Chemical Vapor Deposition; Kai Fu, Houqiang Fu, Hanxiao Liu, Shanthan Reddy Alugubelli, Tsung-Han Yang, Xuanqi Huang, Hong Chen, Izak Baranowski, Jossue Montes, Fernando A. Ponce and Yuji Zhao; Arizona State University, Tempe, Arizona, United States.

Gallium nitride (GaN) power devices have become one of the most promising candidates for applications in power electronic systems, offering remarkable improvements in energy conversion efficiency, switching frequency, and system volume. As one of the most important fundamental building blocks of semiconductor electronic devices, p-n junctions, created by doping methods using ion implantation, diffusion of dopants, or epitaxy, are also of great importance in fabricating GaN power devices. However, they are still difficult to implement for GaN, especially for p-type doping. It was found that GaN was not very resistant to ion beam disordering and this problem became more severe at higher dose ion implantation. For diffusion of dopants, the understanding of this process in GaN is also in its infancy. Epitaxy on GaN substrates may partly solve these issues due to the reduced dislocation density in the materials and doping during growth is still the most effective way to get well-controlled doping. Moreover, to fabricate high-performance GaN power devices and integrated-circuits, selective-area doping is indispensable. However, some physical mechanisms are still not clear, especially on regrown p-GaN. In this work, to mimic selective-area doping, p-GaN was regrown on an etched GaN surface on GaN substrates by metalorganic chemical vapor deposition. Vertical GaN-on-GaN p-n diodes were fabricated, where the etch-then-regrowth process was used to fabricate the devices. The crystal quality of the sample after each epitaxial step was characterized by X-ray diffraction, where the etch-then-regrowth process led to a very slight increase in edge dislocations. A regrowth interfacial layer was clearly shown by transmission electron microscopy. Strong electroluminescence was observed with three emission peaks at 2.2 eV, 2.8 eV and 3.0 eV, respectively. The 2.2 eV peak was related to the well-known yellow luminescence of GaN, which is due to capture of conduction band electrons by a deep acceptor level centered at 2.2 eV below the conduction band edge (CBE). The 2.8 eV peak originated from the donor-acceptor pair (DAP) luminescence, i.e., the transition from a deep donor level (~0.4 eV below the CBE) to the Mg acceptor level which is ~0.2 eV above valence band edge (VBE). The forward current density increased slightly with the increasing temperature, while the reverse current density was almost temperature independent indicating tunneling as the reverse transport mechanism. This result is very similar to the reported Zener tunnel diode comprising a high doping profile at the junction interface. High levels of silicon and oxygen concentrations were observed at the regrowth interface with a distribution width of ~100 nm. This work provides valuable information of p-GaN regrowth and regrown GaN p-n diodes, which can serve as an important reference for developing selective doping for advanced GaN power electronics for high voltage and high power applications.

4:00 PM EP09.09.08
The Study on Inhomogeneity of GaOx Schottky Barrier Diodes by Modified Thermionic Emission Model; Tsung-Han Yang, Houqiang Fu, Hong Chen, Xuanqi Huang, Jossue Montes, Izak Baranowski, Kai Fu and Yuji Zhao; Arizona State University, Tempe, Arizona, United States.

Gallium oxide, one of the promising ultrawide-bandgap material, has recently attracted considerable interest because of its potential for high power application and cost-effective growth. Its large bandgap (4.8 eV) and high breakdown electric field (8 MV/cm) result in superior energy density capabilities. The critical field strength of gallium oxide is more than 20 times that of silicon and more than twice that of silicon carbide and gallium nitride. The BFOM of gallium oxide is at least four times larger than those of SiC and GaN, indicating its great potential for high power application. Another advantage of gallium oxide is the availability of cost-effective single-crystal substrates. The edge-defined film-fed growth (EFG) method, described by Labelle and Mlavsky, is one of the main methods to grow large-sized β-Ga2O3 substrates, as its relatively low cost and scalability make it aptly suited for use in mass production. Electronic devices such as field effect transistors (FETs) and Schottky barrier diodes (SBDs) and optoelectronic devices such as solar-blind

4:00 PM EP09.09.09
The Study on Inhomogeneity of GaOx Schottky Barrier Diodes by Modified Thermionic Emission Model; Tsung-Han Yang, Houqiang Fu, Hong Chen, Xuanqi Huang, Jossue Montes, Izak Baranowski, Kai Fu and Yuji Zhao; Arizona State University, Tempe, Arizona, United States.
Photodetectors fabricated on the β-Ga$_2$O$_3$ substrates have been reported. However, the mechanism of the temperature-dependent performance of these devices is still not very clear. The non-ideal properties including (i) temperature-dependent Schottky barrier height and (ii) ideality factor and (iii) unreasonably small extracted Richardson constant cannot be easily explained by traditional thermionic emission theory with a homogeneous barrier. Similar behavior has been observed for a-IGZO, nanocrystalline ZnO, and ZTO. As a result, in this paper, a modified thermionic emission model over an inhomogeneous barrier having a voltage-dependent barrier height has been investigated and used to explain these non-ideal phenomena.

4:15 PM EP09.09.09
Optimizing Spin Hall Conductivity in Materials for Low Power SOT-MRAM
Derek Stewart$^1$, Wen Fong Goh$^3$ and Martin Gradhand$^1$; 1 San Jose Research Center, Western Digital; San Jose, California, United States; 2 Physics Department, University of California, Davis, Davis, California, United States; 3 HH Wills Physics Laboratory, University of Bristol, Bristol, United Kingdom.

While current magnetic RAM devices have demonstrated impressive speed, endurance, and retention, the power requirements for this technology still represent a key challenge for its widespread adoption. The ability of a spin Hall material to switch the spin orientation of a neighboring magnetic layer could serve as a key element in future low-power spin-orbit torque (SOT) MRAM devices. The spin Hall angle is given by the ratio between the induced transverse spin Hall conductivity due to spin-orbit interactions and the longitudinal electrical conductivity. While a high spin Hall angle is important, it is also critical to ensure low electrical resistance in order to develop energy efficient memory. In this work, we use first principle approaches to calculate the spin Hall conductivity in leading spin Hall materials: β-W (A15), β-Ta, and Pt-based alloys. We first calculate and confirm the fully relativistic Fermi surfaces and band structures for these materials using multiple ab-initio approaches, including plane wave formalisms (VASP, Quantum Espresso [1, 2]) and a relativistic Korringa-Kohn-Rostoker (KKR) approach [3]. The intrinsic spin Hall conductivity is calculated using two independent implementations of the Kubo formula based on the Berry curvature [4, 5]. For β-W, we predict intrinsic spin Hall angles ranging from 0.24 (bulk) to 0.45 (film) in excellent agreement with experiments [7, 8]. The spin Hall conductivity in β-W is sharply peaked just below the Fermi energy and the origin of this peak can be traced to closely spaced spin-orbit split bands near the Fermi energy. We will discuss how symmetry breaking in the A15 crystal phase leads to enhanced spin Hall conductivity and how this could potentially be leveraged in other materials. Calculations for Ta doped β-W show that the spin Hall conductivity peak can be shifted to the Fermi energy, boosting the spin Hall conductivity and angle by ~20%. This finding agrees with results from a recent study based on plane wave projection to maximally localized Wannier functions [9]. Since oxygen and nitrogen are often used to stabilize the metastable β-W, we also examine the potential impact of these dopants on the electronic structure and spin Hall conductivity. Predicting the spin Hall conductivity in the β-Ta is particularly challenging computationally due to the large tetragonal unit cell with 30 atoms. Our spin Hall conductivity predictions for β-Ta are in good agreement with experiments and our results indicate that the local β-Ta atomic environment could be similar to that found in the A15 phase. Finally, using a virtual crystal approximation, we examine the intrinsic spin Hall conductivity in Pt based binary alloys. We find good agreement with measured spin Hall conductivity for most of the composition range and the deviations from the predicted values can be traced to skew scattering contributions. Taken together, these different materials systems provide important insight on how the crystal structure and doping in a material can be tailored to boost spin Hall conductivity.


4:30 PM EP09.09.10
Study of Magnetization Precession in Perpendicularly Magnetized W/CoFeB/MgO Films Using TR-MOKE
Dustin M. Lattery, Delin Zhang, Jie Zhu, Xudong Hang, Paul A. Crowell, Jian-Ping Wang and Xiaojia Wang; University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

Perpendicular magnetic materials with low damping constant and high thermal stability have great potential for realizing high-density, non-volatile, and low-power consumption spintronic devices, which can sustain operation reliability for high processing temperatures. In this work, we study the Gilbert damping constant (α) of perpendicularly magnetized W/CoFeB/MgO films with a high perpendicular magnetic anisotropy (PMA) and superb thermal stability. The α of these PMA films annealed at different temperatures (T_anneal) is determined via an all-optical Time-Resolved Magneto-Optical Kerr Effect (TR-MOKE) method. We find that α of these W/CoFeB/MgO PMA films decreases with increasing T_anneal, reaches a minimum of α ~ 0.015 at T_anneal ~ 350 °C, and then increases to 0.020 after post-annealing at 400 °C. The minimum α observed at 350 °C is rationalized by two competing effects as T_anneal becomes higher: the enhanced crystallization of CoFeB and dead-layer growth occurring at the two interfaces of the CoFeB layer. We further demonstrate that α of the 400 °C-annealed W/CoFeB/MgO film is comparable to that of a reference Ta/CoFeB/MgO PMA film annealed at 300 °C, justifying the enhanced thermal stability of the W-seeded CoFeB films. Further, we discuss the dependence of the TR-MOKE signal on the magnitude and angle of the applied field, by utilizing a numerical algorithm based on the Landau-Lifshitz-Gilbert equation. The optimized operational conditions that produce the largest TR-MOKE signals are predicted and confirmed.

4:45 PM EP09.09.11
Indium Tungsten Oxide Thin Films for Flexible High Performance Transistors and Neuromorphic Electronics

Thin film transistors (TFTs) with high electrical performances (mobility > 10 cm$^2$/Vs, $V_{th} < 1$ V, $SS < 1$ V/decade, on/off ratio > $10^6$) obtained from the silicon and oxide-based single-crystalline semiconductor materials require high processing temperature and hence not suitable for flexible electronics. Amorphous oxide based transparent electronic devices are attractive to meet emerging technological demands where crystalline oxide/silicon-based architectures cannot provide a solution. Here, we tackle this problem by using a novel amorphous oxide semiconducting material—namely indium tungsten oxide (IWO)—as the active channel in flexible thin film transistors (FTFTs). Post-annealing at temperature at as low as 270°C for a-IWO thin films deposited by RF sputtering at room temperature could result in smooth morphology ($R_m\sim 0.42$ nm), good adhesion and high carrier density ($n \sim 7.19 \times 10^{15}$ cm$^{-3}$). Excellent TFT characteristics of flexible devices could be achieved with linear field effect mobility ($\mu_{FE}$) of 25.86 cm$^2$/Vs, sub-threshold swing SS < 0.30 V/decade, threshold voltage $V_{th} < 1.5$ V, on/off ratio $I_{on}/I_{off} > 5.6 \times 10^6$ at 3V and stable operation during bending of the FTFT. Additionally, IWO TFTs were implemented as synapses, the building block for neuromorphic computing. Paired-pulse facilitation (PPF) up to 138% was observed and showed an exponential decay resembling chemical synapses. Utilizing this characteristic, high-pass dynamic temporal filter was devised providing increased gain from 1.55 to 21 when frequency was raised from 22 to 62 Hz. The high performance and stability of flexible TFTs obtained with IWO films demonstrate their promise for low voltage electronic applications.

SYMPOSIUM EP10

Heterovalent Integration of Semiconductors and Applications to Optical Devices
April 24 - April 25, 2019

Symposium Organizers
Isaac Hernandez-Calderon, CINVESTAV
David Smith, Arizona State University
2:45 PM BREAK

SESSION EP10.01: Heterovalent II-V/III-V Integration
Session Chairs: Isaac Hernandez-Calderon and Achim Trampert
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 226 B

1:30 PM *EP10.01.01
Semiconductors Heterovalent Interfaces and Integration Yong-Hang Zhang; Arizona State University, Tempe, Arizona, United States.

Abstract: Semiconductor electronic and optoelectronic materials and devices have experienced very rapid development for more than half a century. The recent progress in development of quantum materials and their applications in quantum computing, communication, and sensing also calls for in-depth understanding of interfaces between dissimilar semiconductors, semi-metals, and superconductor, and broad exploration of new heterovalent integration of these materials from different families. Thin layer quantum structures and their interfaces consisting of materials families such as group II-VI (MgZnCdHg(SeTe), III-V (AlGaan)(PAsSb)), IV-V (SiGeSnPb), and IV-VI PbSe(SeTe) grown on GaAs, InP, GaSb, InAs and InSb substrates offer a very broad spectrum of interface configurations, alloy combinations and their quantum properties for both fundamental physics study and device applications. This talk will focus on the latest progress in the MBE growth of these heterovalent structures and their potential applications in quantum materials research, solar cells, midwave IR light emitting devices, and photodetectors.

2:00 PM *EP10.01.02
Narrow Linewidth Semiconductor Disk Lasers and Progress Towards ZnCdMgSe Vertical Gain Structures George Chappell1, Brynmor Jones1, 2, Thor Garcia1, Maria Tamargo1 and Jennifer Haste1; 1University of Strathclyde, Glasgow, United Kingdom; 2Fraunhofer Centre for Applied Photonics, Glasgow, United Kingdom; 3The City College of New York, New York, New York, United States.

Optically-pumped semiconductor disk lasers (SDLs), also commonly known as vertical external cavity surface-emitting lasers (VECSELs), are of particular interest for applications that require high spatial and/or spectral brightness at novel wavelengths. A typical SDL gain structure consists of a multi-quantum-well resonant period gain region on a monolithic distributed Bragg reflector (DBR). This gain mirror is then optically-pumped and aligned within a conventional air-spaced laser resonator. With their relatively high output power (multi-Watt) and high finesse cavities, SDLs are ideally suited for narrow linewidth operation, demonstrating low frequency and intensity noise; properties we are currently exploiting to develop visible SDLs with sub-kHz linewidth for application in quantum technology, specifically atomic clocks. SDLs have been demonstrated from the deep ultraviolet to the mid-infrared via a combination of III-V semiconductor bandgap engineering and intracavity nonlinear frequency conversion; however, direct emission at wavelengths around the so-called ‘green-gap’ would offer many advantages in size, efficiency, and tunability as well as removing a nonlinear conversion step towards the UV.

With the advent of high power GaN pump lasers, un-doped II-VI materials show promise for optically-pumped gain structures in this spectral region, and there is already a large body of work on II-VI-based vertical structures on GaAs, including high quality DBRs. Our interest is in ZnMgCdSe on InP substrates, which offers optical gain from the blue to the red. Optically-pumped edge-emitting lasers in the blue-green, and red were previously demonstrated by the Tamargo group. DBRs are in development with the possibility of using the superlattice technique that has proved successful for material lattice-matched to GaAs; however, SDLs need not have a monolithic DBR if the quantum well gain region can be transferred to a transparent substrate. Here we present an overview of our recent work in visible narrow linewidth SDLs, and our progress on the design, growth, processing and characterization of ZnCdMgSe multi-quantum well gain structures, including transfer of gain regions to single crystal diamond windows.

2:30 PM EP10.01.03
Strategies for Analyzing Non-Common-Atom Heterovalent Interfaces—The Case of CdTe-on-InSb Esperanza Luna1, Achim Trampert1, Yong-Hang Zhang2, Martha McCartney3 and David J. Smith1; 1Paul-Drude-Institut, Berlin, Germany; 2Arizona State University, Tempe, Arizona, United States.

The selective combination of closely lattice-matched group II-VI/group III-V semiconductors offers potential benefits due to the wide range of band-gap energies achievable and novel effects at the interface arising from the valence-mismatch. Very little has been done so far to exploit these opportunities, in part due to challenges in determining the structure and properties of the interface, for instance using scanning transmission electron microscopy (STEM) techniques.

The combination of CdTe (II-VI) and InSb (III-V) implies the existence of a heterovalent non-common-atom (NCA) interface which must contain mixtures of II-V and/or III-VI bonds. Because of the close atomic numbers of the constituent elements, high-angle annular dark-field (HAADF) and large-angle bright-field (LABF) STEM, as well as electron energy-loss spectroscopy measurements are inherently difficult to interpret. In contrast, we show here that the use of the 002 dark-field (DF) imaging technique emphasizes the interface location by comparing differences in structure factors between the two materials. Additionally, detailed analysis of the digitized 002 DF TEM intensity allows quantification of the interface width to be made, which further allows the possibility to address questions such as exploring the presence of (unintentional) interfacial layers or mechanisms governing the interface formation in these complex valence-mismatched interfaces. The approach adopted here for the interface analysis relies on the comparison of experimental and simulated contrast profiles at the CdTe-on-InSb interface, where different functional dependences (e.g. sigmoidal function, error function) for the atomic species are assumed. Since the contributions of the III- (II-) and V- (VI-) elements need to be separately considered, the cation and anion intermixing are independently determined. Furthermore, information at the monolayer level can be unambiguously obtained. Finally, our study reveals that the CdTe-on-InSb interface is structurally abrupt to within about 1.5 nm (10-to-90%-criterion).

The method is of general applicability, and it will be applied in the future to other NCA heterovalent interfaces. Hence, it opens a new route for investigation of the long aimed correlation between the interface-related electronic properties and transport phenomena and the interface characteristics.

2:45 PM BREAK

SESSION EP10.02: Heterovalent and Isovalent Integration
Session Chairs: Isaac Hernandez-Calderon and Esperanza Luna
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 226 B

3:30 PM *EP10.02.01
Development of Scalable Si-Based Composite Substrates for Various Optoelectronic Materials at 6.1 Å and 6.4 Å Yuanping Chen; U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Silicon CMOS has become a gold standard as the signal processor for various optoelectronic devices. Therefore, it is highly desirable to have the devices built on the sensing materials epitaxially grown on Si base composite substrates to ensure reliable low temperature operation due to thermal match between the device structure and Si CMOS. In
addition, super scalability of readily available Si substrate enables fabrication of large area and low cost optoelectronic devices. However, due to the very large lattice mismatch between semiconductors at 6.1 Å and 6.4 Å and the Si substrate (about12% and 19% respectively), a buffer layer has to be used to bridge the gap and to accommodate the mismatch dislocations generated at the interface, as shown in figure 1. Considering the advantageous properties of II-VI material in accommodating mismatch dislocation, we choose ZnTe and CdTe as buffer materials to fabricate ZnTe/Si and CdTe/Si composite substrates for optoelectronic materials at 6.1 Å, such as GaSb or InAs base-type-2 superlattice and HgCdSe IR material, and at 6.4 Å, such as HgCdTe IR material, respectively. Furthermore, a small percentage of Se added into either the ZnTe or CdTe matrix will create a composite substrate lattice matching to the targeted optoelectronic materials, which will minimize the dislocations generated in device material. In this paper we will present our systematic studies on the molecular beam epitaxial (MBE) growth of Cd(se)Te/Si and Zn(se)Te/Si with emphasis on the techniques to reduce dislocations generated in the buffer layer as well as on control of Se concentration to achieve lattice matching with over-grown device layer. The quality of the buffer layers were evaluated by x-ray diffraction, transmission electron microscopy and etched pit density. Our results indicate a buffer layer of CdTe or ZnTe with dislocation as low as 10^4 cm^-2 can be grown on Si substrate. Photodiodes fabricated from Hg_0.9Cd_0.1Te grown on a lattice-matching CdSe/CdTe composite substrate exhibit excellent I-V characteristics [1]. The results validate the CdSe/CdTe/Si as a low-cost, scalable and high quality composite substrate for optoelectronic device at 6.4 Å.

4:00 PM EP10.02.02 Growth of Silicon Doped InAs by Atomic Layer Epitaxy Guy M. Cohen,1 Marinus Hopstaken,1 Michael R. Saccomanno1, William T. Spratt1, Sanghoon Lee1, Christian Lavoie2, Rene T. Mo1, Doron Cohen Elias2, Shmuel Saad2, Arnold Bloom2, Sergey S. Shusterman2, David Memram2 and Moti Katz2,† IBM T.J. Watson Research Center, Yorktown Heights, New York, United States; 2The Israel Center for Advanced Photonics, Sorokq Nuclear Research Center, Yavne, Israel.

We report the growth of in-situ silicon doped InAs layers over In_{0.5}Ga_{0.5}As/In/In/Si by atomic layer epitaxy (ALE). The use of ALE enables us to obtain uniform smooth layers with Si doping concentration in excess of 5E19 cm^-2 at growth temperatures of 400°C. This high doping level is typically hard to achieve with metal organic chemical vapor deposition (MOCVD) at similar growth temperatures. Furthermore, the growth was selective to silicon dioxide, with deposition taking place only over semiconductor surfaces. We have used doped barium sulphide (TBA) as a source for As, trimethylindium (TMin) as a source for In, and silane (SiH4) as a source for Si. ALE is also a unique tool for investigating amphoteric doping with silicon (a group IV element) in III-V materials. We designed two ALE cycles for growing Si doped InAs. The first cycle comprised of the following pulses: (1) TBA, (2) purge with H2, (3) TMin + SiH4, (4) purge with H2.

The second cycle comprised of:

1. TBA + SiH4, (2) purge with H2, (3) TMin (4) purge with H2.

In the first ALE cycle, Si doping was introduced with the group-III element, while in the second ALE cycle, Si doping was introduced with the group-V element. Secondary-ion mass spectrometry (SIMS) showed that incorporation of Si was 20x larger when Si was introduced with group-III. Furthermore, while the growth rate as a function of TMin pulse length saturates, longer SiH4 pulses did result in higher doping for pulse durations we studied.

4:15 PM EP10.02.03 High-Hole Mobility (500 cm2/Vs) Polycrystalline Ge Thin Film on a GeOx Coated Flexible Plastic Substrate Toshifumi Imao, Kento Moto, Takashi Suemasu and Kaoru Toko; University of Tsukuba, Tsukuba, Japan.

Ge on insulator (GOI) technology has been widely studied for lowering the fabrication cost and improving the device performance of Ge metal-oxide-semiconductor field-effect transistors. Solid phase crystallization (SPC) is a simple method to directly form polycrystalline Ge (poly-Ge) thin films on glass substrates at low temperatures [1]. Recently, we found that the control of the atomic density of an amorphous Ge precursor for SPC dramatically enlarged the grain size and updated the maximum value of hole mobility of semiconductor thin film on insulators [2-4]. The electrical properties of these Ge layers greatly depended on the film thickness, suggesting that the underlying interface influences the electrical properties [3]. Generally, it is known that the grain size of the Ge layer changes depending on the type of the underlayer [5,6]. In this study, we investigated the effect of the underlayer insertion on the SPC-Ge and broke the record with a hole mobility of 560 cm2/Vs by employing a GeO2 underlayer. Furthermore, we achieved a hole mobility of 500 cm2/Vs on even a plastic substrate.

To investigate the effects of the underlayer material, we prepared a 50-nm-thick insulating layer (SiN, Al2O3, GeO2) on a SiO2 glass substrate using RF magnetron sputtering. After that, amorphous Ge (a-Ge) precursors were prepared using a Knudsen cell of a molecular beam deposition system (base pressure: 5 x 10^-7 Pa) while heating the samples at 150°C. The thickness of the a-Ge layer was ranged from 100 to 600 nm. The samples were then loaded into a conventional tube furnace in a N2 atmosphere and annealed at 450°C for 5 h to induce SPC. After that, we performed post annealing (PA) at 500°C for 5 h to enhance the electrical properties. For comparison, samples without forming an insulating layer were also prepared. In addition, a sample with a GeOx coated plastic (polymide) substrate was prepared, which was annealed at 375°C for 150 h. After annealing for SPC, the grown Ge layers were evaluated by using electron backscattering diffraction (EBSD) analysis. The electrical properties of the SPC-Ge layers were evaluated using Hall effect measurements.

The EBSD images showed that the crystal grain size of the Ge layer on glass varied depending on the type of the underlayer. This suggests that the frequency of Ge nucleation was changed because of the change of the underlayer material. The Hall effect measurements showed that the larger grain size provided the lower hole density and the higher hole mobility. From the above results, we found that the GeO2 underlayer provides the largest grains and the highest hole mobility among the underlayer materials. The 400-nm-thick Ge on a GeO2 coated glass substrate, annealed at 450°C, exhibited a hole mobility of 440 cm2/Vs. Furthermore, the hole mobility was improved to 560 cm2/Vs by the PA at 500°C due to the defect compensation effect.

Based on the above results, we prepared a 400-nm-thick Ge layer on a GeO2 coated plastic (polymide) substrate, and induced SPC at 375°C. The resulting Ge layer exhibited a grain size of 9.1 μm and a hole mobility of 500 cm2/Vs. This hole mobility is the highest record among that of semiconductor thin films directly synthesized on a plastic substrate. This achievement will give a way to realize advanced electronic and optical devices simultaneously allowing for high performance, inexpensiveness, and flexibility.


Solar cells based on heterojunction with intrinsic thin layer (HIT) technology use heterojunctions to optimize the collection of photogenerated carriers. The silicon heterojunction (SHJ) solar cell design uses a combination of doped amorphous silicon [a-Si:H(p/n)] and intrinsic amorphous silicon [a-Si:H(i)] to form a contact that is selective to either electrons or holes. This design leads to a heterointerface which is formed between amorphous silicon-a-Si:H and crystalline silicon-c-Si which is critical to overall device performance; and consequently, it is imperative to understand the underlying physics that governs that transport.

There is still debate about the impact of the a-Si:H(i) layer and the defects in this layer on transport and on overall device performance. There have been experimental studies that have attempted to study the modes of hole transport through the a-Si:H(i) layer for a a-Si:H(p) emitter SHJ solar cell. Taguchi et al. did temperature dependent IV measurements and inferred that a multi-phonon process must be dominant[1]; Crandall et al. performed transient capacitance experiments and concluded that ‘hopping’ transport is the dominant mode transport [2]. However, many simulation studies which use commercial simulation tools are unable to rigorously study transport while studying cell level properties [3,4]. In this paper we explicitly simulate the transport of holes across the a-Si:H(i)/c-Si heterointerface and correlate it to overall device performance. We use a traditional drift-diffusion model to calculate the electric fields and potentials within the device for device operating conditions. Previously, we have also developed an ensemble Monte Carlo solver that calculates the energy of photogenerated carriers at the heterointerface [5]. Then we use a kinetic Monte Carlo (KMC) to explicitly study hole transport through the a-Si:H(i) layer for particular device operating conditions. This method allows us to explicitly study transport mechanisms such as multi-phonon injection/extraction, defect assisted ‘hopping’
transport, Pool-Frenkel emission, thermionic emission etc.

In this work we used the KMC to simulate hole transport across the a-Si:H(i) layer. This was done for various device conditions. Our simulations indicate that increasing a-Si:H(i) layer thickness (4 nm → 18 nm) at 300 K at short circuit condition leads to an increase in average collection time for holes (10⁻² → 10⁻¹ sec). However, the average collection time saturates at higher a-Si:H(i) layer thicknesses (>12 nm). Simulations were also conducted for varying temperature, interface defect density, optical phonon energy, and at open-circuit condition and maximum power point conditions for solar cells. We also replicated an experimental study (given in ref 2) by simulating time dependent carrier decay across the a-Si:H(i) barrier and obtained very similar trends. Our simulations in conjunction with the experimental studies strongly indicate that the hole are collected via 'hopping'. We are currently trying to quantitatively correlate our transport simulations to device performance parameters such efficiency, fill factor and open-circuit voltage.


4:45 PM EP10.02.05 Twin Boundaries in GaP Nanowires—Electronic Structure and Optical Properties Divyanshu Gupta1, Nebile Isik Goktas2, Amit Rao2, Ray LaPierre2 and Oleg Rubel1, 1Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; 2Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada.

Semiconductor nanowires are used in optoelectronic devices, such as light-emitting diodes, lasers, solar cells, and photodetectors [1]. Formation of multiple twin boundaries during the growth of nanowires is very common. However, the effects of these planar defects on the electronic and optical properties of nanowires are not very well understood. It is unclear whether twin boundaries act as recombination centers and if they introduce any barriers/traps for charge transport.

Here, we combine ab initio electronic structure calculations with experimental techniques to study these effects [2]. Twin boundaries in GaP are shown to act as an atomically-narrow plane of wurtzite phase with a type-I band alignment homosctructure. Presence of twin boundaries leads to the introduction of shallow trap states. Trapped optical excitations have a weak, but finite dipole matrix element. It results in optical transitions that are otherwise suppressed in the indirect band gap GaP. Sub-band gap peaks observed in photoluminescence studies of GaP nanowires are attributed to twin boundaries and extended regions of wurtzite GaP. Implications of the presence of twin boundaries on the performance of nanowire-based devices will be discussed.


SESSION EP10.03: Poster Session: Heterovalent Integration of Semiconductors and Applications to Optical Devices

EP10.03.01 Fabrication of a One-Dimensional AlGaNpGaAs Microrod via a Top-Down Approach with Micro-Engineering Gang Yeol Yoo1, Joongho Lee2, Yun Jae Fo2, Woong Kim1 and Young Rag Do2; 1Korea University, Seoul, Korea (the Republic of); 2Kookmin University, Seoul, Korea (the Republic of).

The importance of studies of various types of III-V based inorganic materials is increasing rapidly due to their attractive properties, such as their thermal, chemical and moisture stability, direct bandgaps, and the high population density nature of these materials and related devices. Moreover, research on micro- or nano-patterned devices with III-V-based materials has been very active owing to the suitability of these materials in commercialized optoelectronic devices given their enhanced lifetimes, high brightness levels, and the high efficiency of novel optoelectronic devices. Here, an AlGaNpGaAs one-dimensional (1D) microrod was fabricated for use in one-directional micro/nano devices by a top-down approach. These 1D microrod structures, which were fabricated by transferring a 1D patterned microsphere as a mask and using plasma dry etching, in this case reactive ion etching (RIE) and inductive coupled plasma (ICP), can be used as a horizontally aligned single microwire device. To fabricate the 1D AlGaNpGaAs microrod, SiO2 thin films deposited by plasma-enhanced chemical vapor deposition (PECVD) were fabricated as microrod arrays to be used a mask for etching the AlGaNpGaAs microrod arrays. In this study, relative etching rates and etching selectivity of the AlGaNpGaAs layer were studied to fabricate vertical aligned III-V microrods. The morphological properties of the AlGaNpGaAs microrod were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A defect analysis was conducted of the dry etching process and the enhanced optical properties of the 1D microrod were analyzed in terms of the photoluminescence (PL) and cathodoluminescence (CL).

EP10.03.02 Theoretical Study of Electronic Properties of Heterovalent Semiconductors Based on SnO2: Vyakhlov Yatskina, Cory K. Perkins and Paul H.-Y. Cheong; Oregon State University, Albany, Oregon, United States.

Sn dioxide (SnO2) belonged to a class of transparent conducting oxide materials and had high transparency in the visible spectrum as well as high electrical conductivity [1]. Pure SnO2 was a n-type semiconductor with a bandgap of 3.6 eV [2]. Structure defects and the presence of impurities had great influence on electronic and optical properties of semiconductors [3]. Doping with heterovalent elements (Sb, F) allowed for modification of the electronic structure: the position of the conduction band minimum and valence band maximum may be shifted, thus altering the bandgap value [4]. Systematic study of heterovalent systems of semiconductors established correlations between composition, structure, and electronic properties, allowing for directed synthesis of new materials with desired properties. First principle simulations provided structure and properties predictions for new compounds. Such simulations were based on the density functional theory (DFT) and could be performed within either the local density approximation (LDA) or by use of the generalized gradient approximation (GGA). Both approaches demonstrated severe underestimation of the bandgap especially in the case of systems with strong d-electron interactions (TiO2, NiO, ZnO, SnO2). Bandgaps obtained with the use of hybrid functionals were close to experimental values, although such simulations were much more computationally expensive and were often incomplete. Our study involved the influence on crystal structure and electronic properties as a result of heterovalent substitutions (up to 10% mol) of Sn and O by Sb, Ta, and F. Using different functionals implemented in VASP code [5], we performed relaxation to find optimized cell parameters for pure SnO2 and its solid solutions with Sb, Ta, and F. While GGA and LDA predict the bandgap of SnO2 with 80% and 60% error respectively, hybrid functional based on Heyd, Scuseria, and Emzerhof (HSE) [6] showed an accurate bandgap value of 3.62 eV in comparison with the experimental value. It was shown that heterovalent substitution of Sn by Sb led to a linear decrease of the bandgap from 3.62 to 3.01 eV for the range of 0 to 11% mol. When Oxygen was substituted by Florine the bandgap decreased to 3.06 eV for 10.2% mol of F. The influence of dopant concentration on the bandgap was linear for all functionals used, indicating this was a possible key to manipulating the bandgap in allovalently substituted Tin Dioxide.

Effect of W⁺⁺ Doping on the Structural, Chemical and Dielectric Properties of Ga₂O₃

Vishal Zade¹,², Mallesh Bandy¹,³, Mohan Raj Rajkumar¹,², Ashley Díaz¹,² and Ramana V. Chintalapalli¹,²,³
¹University of Texas, El Paso, Texas, United States; ²CMR, El Paso, Texas, United States.

Among the wide band gap semiconductors oxides, Ga₂O₃ is explored extensively owing to its wide range of applications such as gas sensing, solar deep UV-photodetector, photocatalytic, high power devices and light emitting diodes etc. There are extensive studies exploring the effect of different dopants in Ga₂O₃ to alter the properties, performance, and new device applications. Here, we report the effect of W⁺⁺ doping on structural, chemical, and dielectric properties of Ga₂O₃. W-doped Ga₂O₃ (Ga₂₋ₓWₓO₃, 0 ≤ x ≤ 0.25, GWO) ceramics were synthesized using solid-state reaction route. Phase and crystal structure of the synthesized compounds were confirmed through X-ray diffraction (XRD) analyses. XRD data of sintered samples reveal that W doped compounds stabilize in monoclinic symmetry similar to Ga₂O₃ for x ≤ 0.1, whereas evolution of secondary phases of unreacted WO₃ begins at x > 0.15. Room temperature dielectric properties of GWO compounds reveal increment in dielectric constant as compared to pure Ga₂O₃. A correlation between structural chemistry, vibrational modes, and dielectric properties of W-doped Ga₂O₃ ceramics is established.

Fabrication of a Remote-Type Single-Package Light-Emitting Diode Using the Mixed Narrowband CaMgAl₃O₄:Eu,Mn Green Phosphor and the KSiF₆:Mn⁺⁺ Red Phosphor for Wide-Gamut White LEDs

Hesoon Kang, Changwok Kim, Keeyong Nam Lee and Young Rang Do; Kookmin University, Seoul, Korea (the Republic of).

In this study, we characterized remote-type single-package (single-PKG) white-light-emitting diodes (WLEDs) using the narrowband CaMgAl₃O₄:Eu,Mn (CaM:Eu,Mn) green phosphor and the line-emitting KSiF₆:Mn⁺⁺ (KSF:Mn) red phosphor in order to enhance the color gamut and luminous efficacy of WLEDs at a correlated color temperature (CCT) of 10000K. We synthesized, optimized and mixed CaM:Eu,Mn phosphors and red-emitting KSF:Mn phosphors. The mixed green and red phosphors were successfully applied to conventional blue LEDs (432 nm) to fabricate a remote-type single-PKG white LED. The luminous efficacies of white and the associated red, green and blue LEDs were measured and found to have reasonable values of ~70, 15, 35, and 5 lm/W, respectively, at 20 mA. This resultant color gamut (~111 %) of a filtered white LED is superior to that of the highest ever color gamut of reported phosphors, such as the sharp γ-AION:Mn,Mg green and KSF:Mn red phosphor (~102.4 %) as well as the commercialized InP/ZnQD-based QDEF for LCDs (~100 %). The wide color gamut of a backlight consisting of an InGaN blue LED, the CaM:Eu,Mn green phosphor, and the KSF:Mn red phosphor can meet the color requirements for backlighting in LCD displays.

Electrical Characterization of Silicon–Nickel Iron Oxide Heterojunctions

James N. Talbert and Wilhemmus J. Geerts; Texas State University, Canyon Lake, Texas, United States.

The market for non-volatile memory is potentially about to hit a brick wall with the flash technology as it might not be scalable beyond the 14nm node. The need for other storage devices is a hot topic in said market, and one possibility is Resistive RAM (ReRAM) devices. These devices can store information through a reversible switch from high to low resistance. Two mechanisms bipolar and unipolar are used to explore the reset process. Bipolar switching uses reverse bias to cause recombination of the oxygen atoms. In this project the applicability of NaₓFe₂O₆₋ₓ in ReRAM devices is being investigated.

Device test wafers with different oxygen concentration and thicknesses were made by reactive RF magnetron sputtering on n and p type Si substrates (×100 test grade 0-100 Ohm.cm). The native oxide was removed using HF 2 minutes before loading the samples in the vacuum chamber. The oxide was deposited by reactive RF co-sputtering using two guns on opposite sides of the sampleholder. To further improve the homogeneity of the oxide layer, the substrate holder was rotated during deposition. Samples were deposited at two different oxygen flow rates. The deposition rate was dependent on the flow and varied from 0.15 (40% O2) to 1.1 (10% O2) A/sec. The Au electrodes were deposited through a stainless steel shadow mask which contained 1312 devices ranging in diameters from 800 micrometers to 50 micrometers with a thickness of 100nm. A quartz coupon was used to shield areas of the Si-wafers from the Ni electrode during the previous deposition step, both Si-Au and Si-NiFeO-Au devices were available for characterization on each wafer. After finishing the total device stack the SiO₂ on the back of the wafers was removed by HF and covered with a 100 nm Aluminum layer using thermal evaporation. A linear four point probe was used to determine the resistivity of the Permalloy Oxide (PyO) thin films on the quartz coupon. Low Oxygen concentration samples yielded a resistivity of 4E5 Ohm cm. High Oxygen concentration samples showed a resistivity of 5E3 Ohm cm. A Summit 12000 probe station of FormFactor and a Keysight B1500A Semiconductor Analyzer were used to characterize the device wafers. Current-voltage relationships were measured at room temperature. This probe system is completely automated which allows for instant access to each of the 1312 devices on the wafer. Heterojunctions on n-type silicon showed strong rectification with Ifor/Irev>50 for low O₂ flow devices and Ifor/Irev>10,000 for high O₂ flow devices. The heterojunction on p-Si showed negligible rectification. As for the devices on p-Si two states were identified, an initial high resistance state and a non-linear IV curve with much larger currents after burn in. The electric characteristics scales with the device area for n-type substrates but not for p-type substrates. Our preliminary results suggest the p-type nature of Permalloy Oxide sputtered at high Oxygen flow.

Electrical Characterization of Silicon–Nickel Iron Oxide Heterojunctions

James N. Talbert and Wilhemmus J. Geerts; Texas State University, Canyon Lake, Texas, United States.

High Resolution Ion Beam Analysis (HR-IBA) combines <111> channeling with 3.039 ± 0.01 MeV (16O, 16O) nuclear resonance. Ga, As, and O coverage are measured to within ±0.1%. HR-IBA before and after etching by matching SIMNRA simulations to HR-IBA spectra. IBA shows that after the etch, oxygen coverage on GaAs decreases 50 ± 4% from 7.2 ± 0.2 ML to 3.6 ± 0.2 ML. The 53.47 stoichiometric ratio of Ga to As remains constant after etching within ±1%. The area surface density shows that decreasing oxygen coverage by a factor two is commensurate with decreasing displacement of Ga and As surface atoms, implicating etching doesn’t corode GaAs or alter stoichiometry.
X-Ray Photoelectron Spectroscopy (XPS) measured oxidation states and uniformity of the surface for C, O, Ga, and As on two locations of two wafers for both native oxide and etched GaAs(100). GaAs native oxides include binary oxides (Ga₂O₃, As₂O₅, As₂O₆), ternary oxides (Ga₅AsO₁₃), and metallic arsenic. The proportion of oxidized Ga increased from 40 ± 1% to 47 ± 1% while the proportion of oxidized As decreased from 21 ± 1% to 19 ± 1%. This change in As oxidation reverses the hydro-affinity of GaAs(100) as the decrease in fully oxidized As increases the amount of unfiled bonds of As, increasing γ \textsuperscript{S}.

In summary, 3LCAA measured a change in GaAs hydro-affinity before and after etching by a factor of two from strongly hydrophobic (γ \textsuperscript{S} = 33 ± 1 mJ/m²) to strongly hydrophilic (γ \textsuperscript{S} = 66 ± 1 mJ/m²). HR-IBA accurately determined to within 0.2 ML decreased oxygen coverage and stoichiometry as a function of wet chemical etching. XPS was then correlated with IBA to establish modifications in the proportion of oxidized Ga and As atoms and in their oxidation states. Modification of oxidation states help explain the dramatic change observed in hydro-affinity.


EP10.03.07
External Piezoelectric Fields Induced Further Trap-Depth Decrease and ML Emissions from ZnS: Mn/PVDF Thin-Film Structures Puilei Wang; State Key Laboratory of Crystal Material, Jinan, China.

ZnS:Mn is one of the most promising luminescence materials for large-scale applications, such as artificial skin, self-diagnosis display, etc. However, the mechanoluminescence (ML) process of ZnS:Mn has been come up for two kinds of mechanisms. In this work, a kind of piezoelectric-assisted structures (ZnS:Mn/PVDF Thin-Film Structures) was designed and investigated for promoting the intensity of mechanoluminescence. As is well-known, ML materials emit light during deformation applying a mechanical stress onto these surface, piezoelectric signals responding to the mechanical stress are generated by ZnS and PVDF as well. The luminescence intensity performance of the ZnS:Mn/PVDF thin-film structures can be increased almost double compared with the pure ZnS:Mn particles. The present work could provide an approach to improving the luminescence intensity of ZnS:Mn ML and it supports the piezoelectrically-induced electron detrapping model for the ML in ZnS:Mn particles as an adjuvant proof.

EP10.03.08
The Gas Sensing Properties of CuSbS\textsubscript{2} Quantum Dots/rGO Composites to Ammonia at Room Temperature Yuqiu Liu; Wuhan University of Technology, Wuhan, China.

The reduced graphene oxide (rGO) has drawn much attention as gas sensing material in the field of gas detection. However, there are still some challenges for its application because of the poor stability and selectivity. Therefore, it is particularly significant for the functionalization of rGO. As a new ternary semiconductor, CuSbS\textsubscript{2} quantum dots (QDs) have many special advantages, such as large specific surface area, tunable band-gap, high carrier mobility, which enables to be applied to enhance the gas sensing properties of rGO. In the present work, rGO sheets are prepared by Hummers method and CuSbS\textsubscript{2} QDs/rGO composites are synthesized by hot injection method, and then CuSbS\textsubscript{2} QDs/rGO composites are self-assembled by a solution method. It is found that there are some wrinkles on the rGO sheets and the average size of CuSbS\textsubscript{2} QDs in the composites is 4.9 nm with the even and dense dispersion on rGO sheets. The gas sensing properties of CuSbS\textsubscript{2} quantum dots responding to the mechanical stress are generated by ZnS and PVDF as well. The luminescence intensity performance of the ZnS:Mn/PVDF thin-film structures can be increased almost double compared with the pure ZnS:Mn particles. The present work could provide an approach to improving the luminescence intensity of ZnS:Mn ML and it supports the piezoelectrically-induced electron detrapping model for the ML in ZnS:Mn particles as an adjuvant proof.

EP10.03.09

Recent advances in nanofabrication techniques have generated innovative approaches to engineer lattice strain in materials, with unprecedented spatial and temporal resolutions. Strain engineering has been demonstrated to drastically improve physical properties of materials and even embed unique functionalities in materials for a broad range of applications, including optoelectronics, microelectronics, multiferroics, two-dimensional materials, functional soft crystals, and more recently, high Tc superconductors and quantum materials. Strain has been implemented in varied forms including lattice misfit strain, thermal strain, phase transition strain and strain from point defects or extended defects such as dislocations. The epitaxial strain induced by the lattice mismatch between the nanostructures and the substrate has opened a door to enhance drive current by controlling the electron and hole mobility in Si-based devices. It has been discussed that it should be possible to enhance electronic properties with strain [1]. The concept of carrier pocket engineering used the influence of strain to engineer the band structure of silicon and germanium based superlattices (SLs) to optimize the electronic transport. Theoretical calculations suggested that the basic features of electron bands for the (Si/Ge) superlattice can be understood in terms of folded average bulk bands, and explained the electronic transport in superlattices based on this hypothesis [2]. This was justified since bands of Si and Ge are very much alike. However, in many of these studies, the effect of interfaces has not been taken fully into account. A complete treatment of electronic transport in a multi-interface system requires solving the complex interplay between the confinement and effect of the interface.

In this work, we investigate electron transport in layered Si/Ge superlattices employing first-principles density functional theory (DFT) and Kronig-Penney (KP) model, in combination with semi-classical Boltzmann transport theory. We report the effect of strain on the electronic structure and transport properties of multilayered nanostructures, by computing electronic properties of superlattices with compositional variability, and substrate induced external strain. The structural non-uniformity induces strain that strongly influences the bonding environment and therefore, the electronic charge densities within these structures. The modified charge densities directly impact electronic band structures. We compute the electronic band structures with DFT and KP model and discuss to what extent superlattice band structures can be thought of as composed of average “bulk” bands. We highlight the importance of interfaces to modify the band structures. It is interesting to note the different interface physics captured by these two models. We discuss the impact of strain on band structures and consequentially, cross-plane electronic transport across the multilayered systems. Our work establishes a direct relationship between the introduction of local and global strain and cross-plane transport in multilayered semiconductor superlattice structures. One representative result from our study is that introduction of positive strain (tension) in the in-plane direction of Si/Ge superlattices leads to significant improvement of the Seebeck coefficient at higher carrier concentrations. The project is funded by the DARPA (DSO) MATRIX program. This work used XSEDE, which is supported by NSF grant number ACI-1053575.


SESSION EP10.04: Heteroevalent Integration I
Session Chairs: Yuanping Chen and Maria Tamargo
Thursday Morning, April 25, 2019
PCC North, 200 Level, Room 226 B

8:00 AM *EP10.04.01
Interface Structure and Defect Formation During III-(Sb,As) Epitaxy on Si(001) Achim Trampert\textsuperscript{1}, M. Niehle\textsuperscript{1}, H. Drube\textsuperscript{1}, J.B. Rodriguez\textsuperscript{2,3}, L. Cerutti\textsuperscript{1,2} and Eric Tournié\textsuperscript{1}; \textsuperscript{1}Leibniz-Institut im Forschungsverbund Berlin, Paul-Drude-Institut für Festkörperelektronik, Berlin, Germany; \textsuperscript{2}Université de Montpellier, Montpellier, France; \textsuperscript{3}CNRS, IES, UMR 5214, Montpellier, France.
The integration of III-V compound semiconductor materials on Si provides a unique opportunity to combine the benefits of advanced optoelectronic materials with the capabilities of established silicon technologies. The direct epitaxial growth of III-V lasers on Si-based electronic circuits appears as very promising, cost-effective and versatile approach. Nevertheless, the heteroepitaxy of very dissimilar materials such as group III-Sb or III-As on Si (001) substrates has been shown for a long time to be challenging by reasons of existing large lattice, thermal and polarity mismatches, which typically result in a three-dimensional growth mode accompanied by the development of high defect densities. Although much progress has been made in recent years on the detailed characterization of the nature of the extended defects and their controlling during growth, a comprehensive understanding of the interface structure and defect formation mechanisms has not yet been achieved. In this contribution, we will present our latest results on interface structures of planar III-Sb layers grown on Si including complex GaSb-based laser structures by molecular beam epitaxy [1]. The origin of misfit and threading defects is unambiguously explored by combining the methods of three-dimensional imaging using electron tomography and scanning transmission electron microscopy and spectroscopy [2,3]. The number and distribution of threading dislocations cannot be made consistent with the concept of their generation during three-dimensional island coalescence on the basis of imperfections in the misfit dislocation networks. Differences in the interface chemistry – GaAs/Si versus AlSb/Si – will be discussed and concepts of defect reduction will be outlined.


8:30 AM *EP10.04.02
Heterovalent Integration as a Tool for Controlling Magnetic Properties of Epitaxial Semiconductor and Metal Films Jacek K. Furdyna; University of Notre Dame, Notre Dame, Indiana, United States.

In this presentation I will discuss three examples of heterovalent integration of semiconductors and magnetic films as a means of controlling their magnetic properties. Let us begin with the alloy GaMnAs, a well known ferromagnetic semiconductor grown by low-temperature molecular beam epitaxy (MBE). The Curie temperature of this material naturally depends on the concentration of the Mn magnetic ions in the crystal lattice. It is well known that the divalent Mn ions incorporated into the GaAs lattice act as acceptors, and that the Fermi level of the holes created by this process puts a limit on how much Mn can be incorporated into the crystal, thus naturally putting a limit on the Curie temperature that can be achieved. [1] We have shown that the hole concentration can, however, be controlled by integrating GaMnAs with Ge (which are very closely lattice-matched), either by epitaxially growing GaMnAs on Ge, or Ge on GaMnAs. [2] This possibility is enabled due to the specific valence band offset that exists between these two materials. As a second example, I will discuss the effect of integrating Fe with either Ge, GaAs or ZnSe. Epitaxial films of bcc alpha-Fe are nearly perfectly lattice matched with these three fcc semiconductors, enabling epitaxial growth of very high quality single-crystal films on these materials. I will show that the magneto-crystalline anisotropy of the resulting alpha-Fe films (a property of major importance in spintronic devices) is strongly related to the semiconductor on which the Fe film is grown. Specifically, it has been demonstrated by using ferromagnetic resonance (FMR) and magnetotransport that magneto-crystalline anisotropy of alpha-Fe films integrated with Ge is perfectly cubic; that it is weakly uniaxial in Fe integrated with ZnSe; and that magneto anisotropy of Fe grown on GaAs is quite strongly uniaxial. [3,4] I will discuss the physical reasons for each of these cases. The effects on magnetic anisotropy of Fe arising from integration with Ge, GaAs or ZnSe become important because of current interest in forming magnetic tunnel diodes and related structures involving GaMnAs and Fe, where GaAs, ZnSe or Ge can be used as non-magnetic barriers between the two magnetic layers. [5]

Finally, I will discuss the interesting case when the ferromagnetic semiconductor GaMnAs is integrated with the topological insulator Bi2Se3. Unlike the preceding two examples, in this case the lattice match is not critical because of the van der Waals forces involved in epitaxial growth of Bi2Se3. It has been shown that such integration has two rather profound effects on the ferromagnetic magnetic properties of GaMnAs. First, the proximity of Bi2Se3 results in a significant decrease of the Curie temperature of GaMnAs. And second, equally as important, this proximity profoundly changes the magnetic anisotropy of GaMnAs and results in a significantly higher magnetic coercivity of GaMnAs. [6] The physical mechanism behind this effect is at present not fully understood, and efforts are continuing to resolve this interesting puzzle.


9:00 AM *EP10.04.03
Epitaxial GaAs/Si Solar Cells Minjoo Lee and Shizhao Fan; University of Illinois Urbana-Champaign, Urbana, Illinois, United States.

Si-based tandem solar cells have become a topic of great interest over the past several years due to the fact that Si single-junction cells are approaching their practical efficiency limits. The highest Si-based tandem efficiency of 32.8% was achieved by bonding a III-V solar cell to Si. Perovskite/Si tandems are next highest in the efficiency race, attaining 27.3% efficiency at the time of writing. The efficiency of epitaxial III-V/Si tandems has also risen rapidly, though remains behind the approaches listed above. In this work I will describe our recent work to separately demonstrate 16.5% efficient GaAs top cells and 7.8% efficient GaAsP-filtered Si bottom cells (both certified by NREL). High short-circuit current density was attained in the Si bottom cell due to strong light-trapping, and our best Si bottom cells produce significantly more current than our best GaAsP top cells. We calculate that when combined, our current-mismatched J3 cells could reach a two-terminal tandem efficiency of 23.9%, and progress towards this goal will be reported.

9:30 AM *EP10.04.04
Tunable Optical and Structural Properties of Ga-Doped ZnO Film with In Situ Doped Atomic Layer Deposition Shang-Yu Tsai1, Chun-Chi Chen2, Cheng Jun Wang1 and Fu-Hsiang Ko1; National Chiao Tung University, Hsinchu, Taiwan; 1National Applied Research Laboratories, NARLabs, Hsinchu, Taiwan.

Recently, Transparent Conducting Oxides (TCOs) were one of the central issue in modern life due to their applications such as flat-panel displays, solar cells, and touch screen displays. For TCOs applied as transparent electrodes, the thin films should own lower resistivity, larger transmittance in visible light range, and enduring stability. Zinc Oxide (ZnO) doped with group-III impurities such as Al and Ga have shown satisfactory optical and electrical properties as a relatively inexpensive alternative TCO material. The common deposition techniques of ZnO thin films including Sputtering techniques, Pulsed Laser Deposition, and so on. These processes needed to change Ga to Zn ratio target for different Ga doping concentration and relatively high temperature to grow well quality ZnO films. In contrast, Atomic Layer Deposition (ALD) system could operate ZnO films easily in different Ga doping concentration at low temperature in great uniformity. Traditionally, ZnO films doped with group-III impurities utilized multi-layer deposition method which deposited several ZnO layer plus one impurity Oxide layer to control impurity doping concentration, the process would cause the restriction of thickness and electrically due to the multi-layer depositing and high resists electric oxide layer.

Here, we developed a method of in-situ doping with flow rate-interruption to grow ZnO thin film by ALD system. The difference between traditional multi-layer growth and in situ doping growth is that Ga, Zn, and O are all in the same layer on the process. The advantages of this method are optimized reaction time, controllable doping concentration, low precursor consumption, high step coverage, stable crystal growth, and controllable film thickness. A (002) highly prefer orientation crystal ZnO thin film was successfully grown on 1 um of amorphous Silicon Dioxide (SiO2) film, which normally promotes random crystal ZnO structure growth. In this study, the in-situ doping with flow rate-interruption method demonstrated better crystalline and enhanced-control doping concentration in ZnO thin films. The in-situ doping flow-rate-interruption ZnO thin films were grown with different TEGa pulsed time at 300 degree Celsius by the ALD system. To understand the composition and structural properties of ZnO thin films, EDS spectrum and Gonio scan were measured. The EDS results showed the different Ga composition ratio of 0.67, 1.28, 1.74, 2.86, and 2.42 at% with the pulsed time of 10, 50, 80, 100, and 130 msec, respectively. The results indicated that Ga doping concentration can be controlled by TEGa pulsed time, and concentration reached saturation after 100 msec. The Gonio scan results showed that the trend of ZnO thin films were from poly crystal structure to (002) highly prefer orientation crystal structure with increasing Ga doping concentration from 0.67 to 1.74 at%. When the Ga doping concentration exceeded 1.74% the film reverted back to poly crystal structure.

In order to realize the electrical and optical properties of ZnO thin films, Hall measurement and Ellipsometry was used. The carrier concentration and electrical resistivity ZnO film was about 10^{19} cm^{-3} and 10^{4} Ω-cm respectively, which was comparable to ITO TCO glass. The steady growth rate of 0.67 to 1.74 at% ZnO thin films were 1.3 A/cycles and roughness were around few nanometers by Ellipsometry fitting, agreed with SEM cross section data. The refractive coefficient of the pure ZnO film was at n=2, however the
coefficient down to $n=1.8$ with Ga doping in visible light at 633 nm. The lowest refractive coefficient was achieved $n=1.76$ at 1.74 at% Ga of GZO film. Interestingly, in contrast to ZnO nearly no absorption, the GZO films strongly absorbed with the extinction coefficient $k=0.7$ at 1.55 um in near-infrared range.

9:45 AM EP10.04.05 Orientation Shift of ZnTe Epilayers Grown on M-Plane Sapphire Substrates by Introducing Nano-Facet Structures Taizo Nakasu and Masakazu Kobayashi; 1,2 Department of Electrical Engineering and BioScience, Waseda University, Tokyo, Japan; 1 Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Shinjuku, Japan.

The growth of single domain ZnTe layers on heterовалent materials is expected for the devices utilizing Electro-Optic (EO) effects. The EO coefficient of ZnTe is one of the highest among the conventional semiconductor materials. (110) or (111) oriented ZnTe layers should be prepared on the heterovalent substrate which does not exhibit the EO characteristics. The transparent substrates should be used since the optical alignment tunings could be simplified. Sapphire was focused on for the substrate, and MBE growth of ZnTe layers have been performed on various substrate surface orientations. It was revealed that the insertion of the low temperature grown thin buffer layers, as well as the high temperature annealing (at 1000 to 1500°C for ten to forty hours) of the sapphire substrate surface to realize atomically smooth surfaces were effective in achieving high crystal quality layers of ZnTe. The single domain ZnTe epilayers with the x-ray rocking curve linewidth of about 400 arcsec were achieved on c-plane (0001) sapphire substrates so far. The nano-facet formation was observed for the m-plane sapphire substrate after the similar annealing. The characteristic nucleation profiles on various nano-facet structures were studied in this study to obtain the insight of the heterovalent interface and the epitaxial relationship. RHEED, AFM and XRD pole figures were mostly used to characterize the interface properties. The un-annealed substrate surface exhibited the featureless surface with the RMS roughness of about 0.3 nm. The m-plane was disappeared after the annealing, and the annealed substrate surface was covered with the periodic nano-facet structure consisting from 5 to 40 nm size of alternately appearing facet structures of r-planes and S-planes. The size of the structure was varied by the annealing condition, and height was about 5 to 10 nm when it was annealed at 1100°C. The height was increased to 50 nm when the annealing temperature was increased to 1300°C. The nucleation profiles of the low temperature buffer layer was drastically varied by those surface structures. RHEED patterns suggested that substrate surfaces of un-annealed and annealed at 1100°C were fully covered with the amorphous layer after 3.5 nm of the deposition at around 100°C. On the other hand, the RHEED pattern of the substrate was barely changed for the 1300°C annealed substrate surface. The low temperature deposition of ZnTe on the r-plane substrate was also monitored in past and the RHEED pattern was barely changed even after the deposition of about 3.5 nm, which suggested that sticking of ZnTe on r-plane sapphire was very poor. It is notable that the deposition of ZnTe buffer layer at such low temperature range was affected by the substrate surface profile. The orientation of ZnTe layers on various surfaces was similarly varied. The (211) oriented ZnTe layer was confirmed when the thick layer was grown on the un-annealed substrate. The orientation was shifted to (331) when the layer was grown on the 1100°C annealed substrate. The epitaxial relationship of ZnTe on S-plane sapphire was studied in past, and the epitaxial relationship of ZnTe (111)/S-plane sapphire was confirmed. The (331) layer formation on the nano-facet structures was observed because this epitaxial relationship was maintained. The poor sticking of ZnTe on the r-plane of nano-facet has resulted in the preferential formation of ZnTe (111) on the S-plane of the nano-facet. The mixture of (211) and (331) ZnTe layer formation was observed for the layer formed on the 1300°C annealed substrate surface. Insufficient formation of the buffer layer has probably caused the deterioration of the crystal quality.

This work was supported in part by the Waseda University Research Initiatives, by the Waseda University Grant for Special Research Projects, and by the Japan Society for the Promotion of Science Research.
(2) Metal-induced layer exchange for large-grained (>50 μm), orientation-controlled Si$_{1-x}$Ge$_x$ (x: 0–1) layers working as a template for compound semiconductors and aligned nanowires [1-6,9,10].

(3) Ultralow temperature synthesis (< 100 °C) of Ge(Sn) for flexible electronics based on inorganic materials [12].


11:30 AM *EP10.04.08

Epitaxial Growth of Transition Metal-Nitrides on GaN
Grace Huili Xing, John Wright, Joseph Casamento and Debdeep Jena; Cornell University, Ithaca, New York, United States.

Several transition-metal nitrides have lattice constants close to that of GaN or AlN and they possess very interesting electronic properties, therefore, offering intriguing possibilities for heterointegration of functional materials on a powerful semiconductor platform. In this talk, I will share our recent work to epitaxially incorporate Nb and Sc in the AlGaN heterostructures. NbN is a well-known superconductor with a transition temperature about 17 K and typically its thin film is deposited using sputtering. Recently, NbN has been epitaxially grown using molecular beam epitaxy on SiC or AlN, which shows an excellent crystallographic registry to the underlying single crystalline substrate. This in turn enabled growth of AlN epitaxially on top of NbN, followed by a GaN high electron mobility transistor heterostructure [Rusen Yan et al. GaN/NbN epitaxial semiconductor/superconductor heterostructures, Nature 555, 183 (2018)]. Alloying Sc into AlN can significantly enhance the piezoelectricity of the resultant thin film, which has led to much improved performance in bulk acoustic wave (BAW) based on AlSeN over AlN. More recently, AlSeN is reported to be even ferroelectric [Simon Fichtner et al. AlSeN: a III-V semiconductor based ferroelectric, arXiv:1810.07968, 2018].

SESSION EP10.05: Novel Structures and Nanostructures
Session Chairs: Marta Tamargo and Yong-Hang Zhang
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 226 B

1:30 PM *EP10.05.01

II-VI Intersubband Quantum Structures Compatible with III-V Technologies
Aidong Shen; Electrical Engineering, City College of New York, New York, New York, United States.

The wide band gap II-VI compounds reported here are Zn$_x$Cd$_{1-x}$Mg$_{1-y}$Se-based, with x and y varying independently from 0 to 1. The large tunability of the band gap energy from 1.75 eV (CdSe) to 3.7 eV (MgSe) (at room temperature) makes the material system very attractive for optoelectronic device applications. One specific application is to fabricate intersubband devices that work at short wavelengths by utilizing the large conduction band offset offered by heterostructures made from the material system. Intervalley scattering, which is typically seen in III-V intersubband quantum structures when short wavelength limit is approached, does not exist in the II-VI material system due to the large energy difference among conduction band energy minima along different directions in wide band gap II-VI semiconductors. This may potentially boost the device efficiency when intraband electron energy transitions are employed to realize light generation, detection or modulation.

We report the growth and properties of Zn$_x$Cd$_{1-x}$Mg$_{1-y}$Se-based II-VI intersubband device structures. The structures were grown by molecular beam epitaxy (MBE) on III-V substrates and therefore can be vertically integrated with III-V devices and are compatible with mature III-V device fabrication technologies. By applying band structure engineering to semiconductor quantum structures, intersubband transition in the optical communication wavelength of 1.55 μm has been realized in metastable CdSe/MgSe coupled quantum well structures. The metastable structures were stabilized by the insertion of thick ZnCdSe spacer layers during MBE growth. Both the MgSe barrier layers thickness and the MgSe coupling layer thickness were optimized to achieve structures with the best intersubband transition characteristics. Quantum-well infrared photodetectors (QWIPs) working in long wave IR and medium wave IR, the two important atmospheric windows, have been fabricated with the Zn$_x$Cd$_{1-x}$Mg$_{1-y}$Se-based II-VI materials. Different QWIP structures covering a relatively very large spectral range can all be grown lattice-matched on InP substrate. This can ensure the high absorption quantum efficiency of the detectors and is especially advantageous for two-color or multi-color QWIPs grown on the same substrate.

2:00 PM *EP10.05.02

Growth Kinetics of Chalcogenide Topological Insulators with Applications to THz Optical Devices
Stephanie Law; Materials Science and Engineering, University of Delaware, Newark, Delaware, United States.

Topological insulators (TIs) are materials with a bulk bandgap crossed by surface states that exhibit linear dispersion and spin-momentum locking. Electrons occupying these surface states have low mass and large Fermi velocity, while the spin-momentum locking leads to a reduction in scattering, since a change in momentum requires a spin flip. Due to their unique band structure, these materials are promising for applications in electronics, spintronics, and optics. The crystal structure of standard TIs like Bi$_2$Se$_3$ is layered: one quintuple layer (QL) of Bi$_2$Se$_3$ is bonded to the next in the c-direction by van der Waals (vdW) bonds. The QLs are strongly bonded in the a-b plane. The weakness of the vdW bonding is a key to their unique electronic properties, which is responsible for the large Fermi velocity and the spin-momentum locking. Due to the QLs being strongly bonded in the a-b plane, a transfer of the metallic phase to a semiconductor phase can be achieved by deposition of an additional capping layer. This is achieved by depositing a second QL of Bi$_2$Te$_3$ on top of the Bi$_2$Se$_3$ film and then subjecting it to the appropriate thermal treatments.

In this work, we show that the use of a trivially-insulating lattice-matched buffer layer between the Bi$_2$Se$_3$ film and the substrate substantially improves the electrical properties of the film. This implies that defects at the film/substrate interface are responsible for much of the unwanted doping in the film despite the use of vdW epitaxy. For TIs grown on sapphire substrates, a trivially-insulating buffer layer of (Bi$_{1-x}$In$_x$)$_2$Se$_3$ (BIS) deposited between the film and substrate reduces the carrier density by more than a factor of two providing a modest increase in mobility. We then applied this technique to TIs grown on GaAs(001), a technologically-relevant substrate. We find that BIS grown on GaAs(001) shows a variety of morphologies. In a narrow growth window, this material shows an extremely flat, hexagonal morphology. This is in contrast to the triangular, wedding cake morphology normally observed for vdW materials. We explain this morphology by examining the site-preferential incorporation of indium and biswath. These films show a substantial decrease in bulk doping and an increase in mobility.

Finally, we show data demonstrating that these materials are excellent THz plasmonic materials. By etching the films into stripes, we are able to excite plasmonic resonances from...
the two-dimensional massless surface electrons. These Dirac plasmons are tunable across the THz band and show exceptionally large effective indices while maintaining long plasmon lifetimes. Films grown using the buffer layer technique show improved lifetimes when compared to films grown directly on sapphire. These materials are therefore extremely promising for THz plasmonic applications like gas sensing or on-chip waveguiding.

2:30 PM EP10.05.03
Electron Microscopic Studies of Epitaxial III-V Materials Laterally Grown Inside Confined Dielectric Templates

Arona Goswami¹, Simone Tommaso Suran Brunelli¹, Brian Markman¹, Daniel Pennachio², Hsin-Ying Tseng¹, Sukgeun Choi³, Aidan A. Taylor⁴, Jonathan Klajmin⁴, Mark J. Rodwell⁵ and Chris Palmstrom⁶, ², ³, ⁴, ⁵, ⁶. ², ³, ⁴, ⁵, ⁶.

Laterally grown III-V epitaxial layers offer multiple advantages over conventional vertically grown layers for fabricating novel semiconductor devices, including choosing growth facets and lowering thickness of fins. To laterally grow epitaxial films, pre-fabricated dielectric templates are used to confine the growth and its direction. This technique was originally developed for Si [1,2] and later used for fabricating III-V semiconductor device structures on Si [3,4]. Such grown nanostructures often suffer from high densities of planar defects like stacking faults and rotational twins. Owing to the sub-micron scale of these embedded epitaxial layers, it is challenging to characterize them. Here we use scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron channeling contrast imaging (ECCI) to characterize the Confined Epitaxial Lateral Overgrowth (CELO) nanostructures grown by chemical beam epitaxy (CBE) and metal organic chemical vapor deposition (MOCVD) on patterned InP (001) and InP (110) substrates. We explore the influence of growth conditions, growth direction, substrate orientations and fabrication procedures on the evolution of facets and the nature of defects observed. We further show growth and characteristics of CELO heterostuctures and superlattice structures.

CBE growths were performed in a VG-Semicon V80H system using phosphine and trimethylindium as precursors with temperatures varying from 470-520 °C. Tilted SEM images show that the facets are dependent on the growth directions. Vertical facets form in structures growing in the <110> direction, while <001> oriented overgrowths show slanted [111]B facets for an InP(110) substrate. Cross sectional TEM images confirm these facets and reveal stacking faults in the [111] planes propagating throughout the growth. While the growth interface shows excellent crystalline quality in most cases, residues from improper cleaning during fabrication lead to formation of irregular facets. Both the (110) and the (001) oriented InP wafers exhibit similar stacking fault densities, while a reduction of the fault density is observed at higher temperatures. High angular annular dark field scanning TEM (HAADF-STEM) images of MOCVD-grown CELO InP/InAs and InP/GaAs heterostructures, as well as InP/InGaAs superlattices show that atomically flat heterojunctions can be realized in the lateral direction using this growth technique. While TEM shows more microstructural detail, ECCI provides an alternate way to qualitatively compare stacking fault densities and twin domains in these structures, with a much faster throughput and minimal sample preparation.

This work was supported by National Science Foundation and Semiconductor Research Corporation.


2:45 PM EP10.05.04
Shape Engineering of InP Nanostructures Grown by Selective Area Epitaxy

Naoyin Wang¹, Xiaoming Yuan¹,², Philippe Caroff¹,², Li Li¹,², Hong Hao Tan¹ and Chenumpati Jagadish¹, ². ¹Department of Electronic Materials Engineering, Research School of Physics and Engineering, The Australian National University, ACTON, Australian Capital Territory, Australia; ²School of Physics and Electronics, Hunan Key Laboratory for Supermicrostructure and Ultrafast Process, Central South University, Changsha, China; ³Microsoft Station-Q at Delft University of Technology, Delft, Netherlands; ⁴Australian National Fabrication Facility ACT Node, Research School of Physics and Engineering, The Australian National University, ACTON, Australian Capital Territory, Australia.

Group III-V semiconductors have been a hot topic for decades due to the fact that they revolutionize electronics and optoelectronics because of their superior physical and optoelectronic properties including high carrier mobility, direct bandgap and band structure engineering capability. Reducing their dimension to the nanometer level not only brings many unique properties, such as large surface-area-to-volume ratio, high aspect ratio, carriers and photons confinement effect, but also enables the miniaturization of devices. Various nanostructures have already been demonstrated and applied to solar cells, lasers, light-emitting diodes, transistors, photothermochemical water splitting, etc. However, to date most efforts on the growth of group III-V nanostructures have been limited to zero- or one-dimensional, such as quantum dots, nanowires and nanotubes. In this work, we demonstrate selective area growth of InP nanostructures, showing the possibility of obtaining several functional nanostructures, capability beyond the limitation of rod-like nanostructure and opening the way to more advanced device geometries.

Selective area growth of InP nanostructures with shapes such as tripod nanowires, nanocrosses, nanomembranes was conducted on InP substrates of different orientations. We investigate the link between the crystal structures, shapes, designed patterns and substrate orientations. For example, we found the crystal phase transitions from wurtzite to zinc blende with increasing nanoslot length along the certain crystallographic directions, indicating a strong correlation between crystal orientation and pattern confinement on the growth mechanism. Moreover, depending on the growth condition and substrate orientation, nanomembranes can be grown either vertically or tilted with respect to the substrate. Our results provide an insightful understanding on the growth mechanism of various InP nanostructures by selective area epitaxy, which favors the achievement of III-V/Si-integrated devices, and opens up many new possibilities for the shape engineering of III-V nanostructures.

3:00 PM BREAK

SESSION EP10.06: Novel Nanostructures

Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 226 B

3:30 PM *EP10.06.01
II-VI Quantum Dots in Nanowires—Tools to Fine-Tune Optical Properties

Edith Bellet-Almaric¹, Marta Orrù²,³, Kimon Moratis²,³, Pamela Rueda-Fonseca²,³, Eric Robin¹, Martien Den-Hertog¹, Yann Gennis², Regis André², David Ferrand¹ and Joel Cibert¹, ²,³. ¹Univ. Grenoble Alpes, CEA, INAC, Grenoble, France; ²Univ. Grenoble Alpes, CNRS, Institut NEEL, Grenoble, France.

A light hole ground state in a quantum dot is highly suitable for single spin optical manipulation due to the versatile optical selection rules [1]. By contrast to Stranski-Krastanov growth which results in flat quantum dots under compressive strain, hence a heavy-hole ground state, the dot-in-a-nanowire configuration is extremely flexible and virtually any material combination, any dot shape and any built-in strain can be realized. It allows one to engineer the hole states in semiconductor dots, and tailor their orbital and spin states: the ground state of a very long (L/D>>1) quantum dots is a light hole.

The vapor–solid–solid (VSS) growth mechanism is well adapted for the size and compositional control. Indeed it can result in compositionally abrupt interfaces and well-controlled aspect ratio by restraining the so-called reservoir effect normally observed in the most common vapor-liquid-solid (VLS) growth method.

ZnTe nanowires incorporating CdTe quantum dots and a ZnMgTe shell were grown by molecular beam epitaxy, at temperatures such that the Au nanoparticles are solid, as observed by HRTEM.

VSS growth still remains much less understood than VLS. In particular, up to now, the role of the catalyst nanoparticle has been mainly overlooked. We show that different epitaxial relations with respect to the substrate coexist: this plays a key role in the nucleation of the nanowires.² For all the growth steps, the effect of temperature appears to be crucial, particularly when considering the growth of CdTe used to form the quantum dot. The sublimation of CdTe and of the evaporation of Cd from the Au nanoparticles is crucial: these two effects must be taken into account in modelling the growth.³
As a result, ZnTe nanowires incorporating very long (L/D>1) and very short (L/D<1) CdTe insertions and a ZnMgTe shell of controlled shape and composition were studied. Combining cathodoluminescence, micro-photoluminescence spectroscopy and autocorrelation measurements, we identify single dot excitation lines corresponding to excitons, biexcitons and possibly charged ones. From linear polarization measurement in emission we found that for elongated quantum dots the intensity of the exciton line becomes stronger for polarization parallel to the nanowire axis, suggesting a light hole type ground state, as confirmed by a more complete study of the emission diagram and of magneto-optical spectroscopy.

References

4:00 PM *EP10.06.02 Transport Properties of MnAs/InAs Heterojunction and InAs Nanowires Formed by Selective-Area Growth Shinjiro Hara1, Matthias T. Elm1,2,3 and Peter J. Klau1,4, Center for Materials Research, Justus Liebig University, Giessen, Germany; 1Institute of Experimental Physics I, Justus Liebig University, Giessen, Germany; 2Institute of Physical Chemistry, Justus Liebig University, Giessen, Germany; 3Research Center for Integrated Quantum Electronics, Hokkaido University, Sapporo, Japan.

Heteroepitaxial structures between semiconducting nanowires and magnetic materials are of great interest for future nanoelectronic and spintronic devices. We have demonstrated the selective-area growth of vertical ferromagnetic MnAs nanoclusters/semiconducting InAs heterojunction nanowires by metal-organic vapor phase epitaxy, which is a catalyst-free bottom-up fabrication method. [1-3] These heterojunction nanowires provide new possibilities and versatility in the creation of novel vertical nanowire devices, e.g., spin-light-emitting diodes, surrounding gate spin-transistors, and THz-emitters. It is crucial to control the MnAs nanocluster formation and improve the size uniformity of heterojunction nanowires for such nanowire devices, and to investigate magnetotransport properties in detail. [4] This invited paper focuses on recent results of the formation and transport characterizations of vertical MnAs/InAs heterojunction nanowires as well as single host InAs nanowires. The vertical heterojunction nanowires were fabricated by endotaxial MnAs nanoclustering after the selective-area growth of host InAs nanowires on partially-SiO2-masked GaAs (111)B substrates. The fabrication processes are described elsewhere in detail. [1, 2] The <0001> direction of hexagonal NiAs-type MnAs nanoclusters is parallel to the <111>-B direction of zinc-blende-type InAs nanowires, as revealed by transmission electron and magnetic force microscopies. After the growth, the nanowires were detached from the substrates by ultrasonic vibration in isopropanol solution, and then, deposited on a SiO2/Si substrate. In order to obtain ohmic contacts, the native oxide layer was removed by Ar milling at 30 W for 60 sec. Afterwards electronic contacts of Ti/Au (25 nm/165 nm) were structured by electron-beam lithography and electron-beam liftoffgraphy. A large positive ordinary magnetoresistance effect up to 150% is observed when the magnetic field is applied in the range between 120 K and 280 K. Angle-dependent transport measurements reveal additional boundary scattering due to the confined transport channel of InAs nanowire. In addition, magnetotransport characterization results of a single host InAs nanowire show universal conductance fluctuations and weak Anderson localization at low temperatures. A single MnAs/InAs heterojunction nanowire, on the other hand, shows only a negative magnetoresistance effect up to 10% at 10 T, which linearly decreases with increasing magnetic field. Refs.: [1] Jpn. J. Appl. Phys. 55, 075503 (2016) open access; [2] Jpn. J. Appl. Phys. 56, 06GH03 (2017); [3] J. Cryst. Growth 464, 80 (2017); [4] Adv. Mater. 26, 8079 (2014) review paper.

4:30 PM EP10.06.03 Characterization of a GaAs(001)/ZnSe/1 ML CdSe/ZnSe Fully-Strained Ultra-Thin Quantum Well with Very Thin ZnSe Barriers Isaac Hernandez-Calderon1, Frantisek Sutara1 and Adrián D. Alfaro-Martínez1, CINVESTAV-IPN, Mexico City, Mexico.

Interface and extended defects severely affect ZnSe/GaAs based heterostructures. Many studies have been devoted to the improvement of this heterointerface interface, and, to the understanding of the defect generation mechanisms during growth and during operation of related optoelectronic devices. The lattice constants of ZnSe (0.5668 nm) and GaAs (0.5653 nm) are very close, however, the slight lattice mismatch produces a small compressive strain parallel to the interface of -0.00265 which is enough to produce misfit dislocations when the ZnSe film reaches the critical thickness h5 ~ 80 nm. On the other hand, due to the large lattice mismatch, h6 for CdSe (0.6077 nm) on ZnSe is only around 3.5 monolayers, after h5, is reached the excitonic emission of CdSe/ZnSe ultra-thin quantum wells (UTQWs) is negligible or even absent. Therefore, under typical growth conditions only 1 to 3 monolayers (MLs) thick UTQWs of CdSe/ZnSe/GaAs(001) with good crystalline quality and intense excitonic emission can be obtained. 1 One ML of the binary refers to the thickness of the cation-anion bilayer given by a/2, where a is the lattice constant. The 1 ML CdSe UTQW represents the thinnest CdSe QW that is possible to grow and some of its physical properties still deserve a detailed explanation and interpretation regarding its high excitonic emission intensity, the quite narrow full width at half maximum (FWHM),2 and the peak energy dependence on growth parameters. Here, we present a study of a nominal 1 ML CdSe UTQW grown by atomic layer epitaxy (ALE) on GaAs(001) at 275 °C within a ZnSe barrier of 20 nm (the barrier adjacent to the substrate, i.e., the buffer layer forming the ZnSe/GaAs heterovalent interface), and a second ZnSe barrier of 25 nm (cap layer). The thickness of each layer and the total thickness of the heterostructure are chosen in such a way that each material is below its critical thickness, so we can obtain a fully strained heterostructure without misfit dislocations, expecting an UTQW with a high-quality crystalline structure. The 19 K photoluminescence spectrum presents an intense excitonic peak at 2.685 eV with a FWHM of 12.3 meV, which is narrower than previous results in CdSe UTQWs grown on relaxed ZnSe barriers.3 The evolution of the excitonic peak as a function of temperature follows very closely the expected slow, monotonic behavior, indicating the absence of QW potential fluctuations due to thickness or composition inhomogeneities. The intensity of the excitonic peak in the photoluminescence experiments decreases rapidly with increasing temperature and it is difficult to observe at room temperature. This can be taken as an indication of the lack of exciton localization caused by potential fluctuations which, as mentioned before, are absent or negligible in the QW structure.

References

4:45 PM EP10.06.04 Control of Axial to Radial Growth of Ge/GeSn Nanowires with H2 Partial Pressure Andrew C. Meng1, Michael Braun1, Colleen S. Fenrich1, Muyu Xue1, Ann F. Marshall2, James S. Harris3 and Paul C. McIntyre1; 1Materials Science and Engineering, Stanford University, Stanford, California, United States; 2Stanford Nano Shared Facilities, Stanford University, Stanford, California, United States; 3Electrical Engineering, Stanford University, Stanford, California, United States.

Germanium-tin is a promising material for novel devices for optical sensing in the mid-IR region. For sufficiently high Sn compositions, the material has a direct band-gap near 0.5 eV, and could have applications either as a detector or as an emiter. The main challenge to growth of high-quality single crystals is the large lattice mismatch of the system (~14% for diamond cubic Sn on Ge) and the low equilibrium solubility of Sn in Ge (~1%). Demonstrations of core-shell Ge/GeSn nanowire structures have shown that it is possible to take advantage of a thin nanowire as a compliant substrate for high quality single crystal growth.1,2 In this work, we show that a Ge nanowire can act as a template for both axial and radial growth of Ge/GeSn heterostructures by controlling H2 partial pressure during CVD growth of GeSn. We are also able to achieve different Sn compositions varying from 2% to 10% using this method as confirmed by STEM-EDS and photoluminescence measurements. With control over axial to radial growth of GeSn heterostructures, a much wider possibility of device architectures can be achieved.

Probing the Phonon Scattering in the Strong Light-Matter Coupling Regime

These findings not only open new possibilities for the optimization of up-conversion processes through the appropriate engineering of suitable FWM processes at single particle level lead us to all-optical switching phenomena in sub-25 fs reflectivity modulations of >0.1 %, where the responsible mechanism points toward to optical Kerr effect. These findings not only open new possibilities for the optimization of up-conversion processes through the appropriate engineering of suitable dielectric materials, remarkably expand the possibility of localizing signals in hybrid nanosystems, but also contribute to an important step toward nanoscale ultrafast all-optical signal processing.

1:30 PM  EP11.01.01
Imaging and Controlling of Hot Electron Dynamics and Nonlinear Upconversion in Plasmonic and Dielectric Nanoantennas Yi Li1, Gustavo Grinblat2, Sabrina Simoncelli2, 1, Michael P. Nielsen2, Rupert F. Oulton2, Emiliano Cortés2, 2 and Stefan Maier1, 2
1Ludwig-Maximilians-Universität München, München, Germany; 2Department of Physics, Imperial College London, London, United Kingdom; 3Department of Physics and Randall Division of Cell and Molecular Biophysics, King’s College London, London, United Kingdom.

The strong light-matter coupling is the core of cavity quantum electrodynamics (CQED), which leads to discoveries of fascinating phenomena in solid state system such as Bose-Einstein condensation and photon blockade. Indirect evidence indicates non-fluorescence processes such as phonon scattering are critical to these phenomena. However, the understanding of such processes remains elusive due to their non-radiative nature smeared by the overwhelming fluorescence in cavities. Here we directly probe phonon scattering based on Raman spectroscopy in the strong coupling regime in a plasmonic cavity embedded with a monolayer MoS2. The studied non-fluorescence process is significantly modified by the hybrid properties of the newly formed half-light half-matter quasiparticles, i.e., polaritons. For the first time, we observe nonlinearly enhanced valley-dependent phonon modes, involved with stimulated lattice vibrations and inter-valley scatterings. This work provides a new perspective to investigate fundamental quantum processes in the strong coupling regime.

2:00 PM EP11.01.02
Probing the Phonon Scattering in the Strong Light-Matter Coupling Regime Xiaozhe Liu1, Jun Yi1, 2, Sui Yang1, Erh-chen Lin1, Yue-Jiao Zhang2, Jian-Feng Li2, Yuan Wang2, Yi-Hsien Lee2, Zhong-Qun Tian2 and Xiang Zhang1
1University of California, Berkeley, Berkeley, California, United States; 2Xiamen University, Xiamen, China; 3National Tsing Hua University, Hsinchu, Taiwan.

The strong-light-matter coupling is the core of cavity quantum electrodynamics (CQED), which leads to discoveries of fascinating phenomena in solid state system such as Bose-Einstein condensation and photon blockade. Indirect evidence indicates non-fluorescence processes such as phonon scattering are critical to these phenomena. However, the understanding of such processes remains elusive due to their non-radiative nature smeared by the overwhelming fluorescence in cavities. Here we directly probe phonon scattering based on Raman spectroscopy in the strong coupling regime in a plasmonic cavity embedded with a monolayer MoS2. The studied non-fluorescence process is significantly modified by the hybrid properties of the newly formed half-light half-matter quasiparticles, i.e., polaritons. For the first time, we observe nonlinearly enhanced valley-dependent phonon modes, involved with stimulated lattice vibrations and inter-valley scatterings. This work provides a new perspective to investigate fundamental quantum processes in the strong coupling regime.

2:15 PM EP11.01.03
Ultrafast Spectroscopy and Transmission Modulation of Vibration-Polaritons Blake S. Simpkins1, Adam Dunkelberger1, Andrea Grafton1, 1, Kenan Fears1, Roderick Davidson2, 1, Wonmi Ahn3 and Jeffrey C. Owutsky1

Vibrational polaritons, composed of strongly coupled cavity optical modes and molecular vibrations, have recently been utilized to modify excited-state dynamics (Nature Communications 2016, 7, 13504) and chemical reaction rates (Acc. Chem. Res. 2016, 49, 2403). Ultrafast vibrational spectroscopy has the potential to reveal how strong coupling modifies vibrational relaxation and energy transfer that can mediate molecular reactivity. Toward that end, we have carried out transient infrared studies on cavity-coupled molecules in solution. Our results have revealed several important phenomena, including (1) the presence of polariton excited states that, in the systems studied, relax more quickly than the molecules in free space; (2) a reservoir of dark states which can dominate the transient spectral response; and (3) ultrafast modulation of the coupled system between the weak and strong coupling regimes, leading to dramatic changes in the transmission and reflection of the system. Ultrafast modulation of transmission spectra is uniquely useful in single pulse studies where saturable absorption is substantially modified due strong coupling effects that result in much larger saturation intensities (~15 x) compared to those measured for the uncoupled molecular system. This behavior has potential applications for nonlinear optical and photonic devices.

2:30 PM EP11.01.04
Coupled Plasmon-Phonon Modes Enhanced Light-Matter Interaction in the Hybrid Ag-MoS2 System Yibu Poudel1 and Arup Neogi2, Physics, University of North Texas, Denton, Texas, United States.

Monolayer molybdenum disulfide (MoS2) is at the focus of current research for different applications ranging from the photovoltaics, photodetection to optoelectronics. The absorption from monolayer MoS2 is four times to that of graphene, but it is still to be optimized to enhance the performance of photonic devices. Multiple excitonic absorption states in the energy range from ultraviolet to visible, and the exceptionally high exciton binding energy excitonic states presents many opportunities to enhance the interactions of incident light to these excitonic states. Hybrid metal–MoS2 structures can be formed with different metals, and tuned with the shape and size of these metal nanostructures to enhance the light-matter interaction by coupling with the specific excitonic energy state as expected. The exciton dynamics followed by the optical excitation and the interaction dynamics such as hybrid exciton formation, exciton-exciton annihilation etc. are strongly influenced due to coupling with the lattice vibrational modes. The plasmon modes, when coupled with phonon modes, control the coherent interaction among the excitonic states as well as the interaction between the excitonic states with the plasmonic states. Here we report the activation of a new vibrational mode in the hybrid silver (Ag)–MoS2 monolayer structure at 35 meV, and the dressing of the Raman mode with the plasmon mode significantly contributes in the light-matter interaction process as measured using the pump-probe spectroscopy. By selecting an optical excitation, which is in resonance to the plasmon modes, the absorption of the incident light is increased due to the enhanced electric field of the localized plasmons. In addition, the new Raman mode in the hybrid structure along with the usual active Raman modes in MoS2 are also resonantly driven by the pulses of the femtosecond fs laser source. The driving field due to resonantly excited plasmons with the pump pulses creates the power broadening of the excitonic optical transitions. Also, the driving field generates quantum coherence effect that significantly modifies the absorption of probe light forming the so-called dark state as illustrated using a density matrix model. There is a strong coherent coupling of the plasmon modes with the excitonic states in MoS2. A hybrid exciton-plasmon band of half-width about 250 meV is formed around A and B excitonic states in the transient absorption spectrum at a delay time of about 500 femtoseconds after the optical excitation. The formation of the hybrid states offers an opportunity to strongly enhance the light-matter interaction and hence improve the performance of optical and electrical devices based on MoS2.
The term “hot electron” is frequently used in the literature to describe electrons in a solid with energies exceeding their thermally-created counterparts at ambient temperature. In plasmonic structures, the nonradiative dephasing of plasmons generates excited (i.e., athermal) electrons in the conduction band of metals and a subsequent electron thermalization process leads to the equilibration of the athermal electrons and the formation of a hot-electron distribution. The high energy nature of athermal and hot electrons enables various of optically-driven processes with fascinating applications in photochemical and photovoltaic devices. More recently, exploring the transient dynamics of such energetic charge carriers has gained a growing attention with the hope for the implementation of active plasmonic platforms. Indeed, the optical modulation of the electron temperature in metals enables the tuning of their refractive index and therefore, allows for the all-optical modulation of the plasmonic response at low light intensity. However, the intrinsic slow decay of the hot-electron temperature via the electron-phonon interaction, impedes ultrafast all-optical modulation in plasmonic structures. In this work, we show that the ultrafast transfer of hot electrons from plasmonic metals to electron accepting materials allows for the sup-picosecond (~190 fs) recovery of the refractive index change in plasmonic metals. Our experimental findings suggest that the activation of hot-electron transfer pathways screen the contribution of electron-photon interactions and instead provide an electron-dominated relaxation mechanism. Through the design of a subradiant, high-Q, and polarization-sensitive plasmonic crystal we demonstrate ultrafast modulation of phase, polarization, and intensity of light in an all-optical fashion.


3:00 PM BREAK

SESSION EP11.02: Optoelectronic Devices
Session Chairs: Milicent Firestone and Jennifer Hollingsworth
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 225 B

3:30 PM *EP11.02.01
Colloidal plasmonic nanocrystals (NCs) are known for their size- and shape-dependent localized surface plasmon resonances. Here we show these plasmonic NCs can be used as building blocks of mesoscale materials. Chemical exchange of the long ligands used in NC synthesis with more compact ligand chemistries brings neighboring NCs into proximity and increases interparticle coupling. This ligand-controlled coupling allows us to tailor a dielectric-to-metal phase transition seen by a 10th in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. We realize a "diluted metal" with optical properties not found in the bulk metal analog, presenting a new axis in plasmonic materials design and the realization of optical properties akin to next-generation metamaterials. We harness the solution-processability and physical properties of colloidal plasmonic NCs to print NC superstructures for large-area, active metamaterials. We demonstrate quarter-wave plates with extreme bandwidths and high polarization conversion efficiencies in the near- to mid-infrared. By combining superparamagnetic ZnFe2O4 NCs and plasmonic Au NCs, we fabricate multifunctional, smart superparticles, which in suspensions switch their polarization-dependent transmission in the infrared in response to an external magnetic field. Finally, by juxtaposing plasmonic NCs and bulk materials, we exploit their different chemical and mechanical properties to transform lithographically defined two-dimensional structures, upon ligand exchange, into three-dimensional structures and use this approach to achieve chiral metamaterials.

4:00 PM EP11.02.02
Near Infrared Absorbing Copper (II) Complexes—Improvement of Absorbance and Hydrothermal Stability Mi-Jeong Kim1, Haeran Kim1, Yong Joo Lee1, Jae-Jun Lee1, Sunjung Byun2, Jae Gwan Chung2 and Ginam Kim1; 1Film Material Laboratory, Material Research Center, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics, Suwon, Korea (the Republic of); 2Platform Technology Laboratory, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics, Suwon, Korea (the Republic of).
Mobile device has developed display, memory, and various sensors for helping human life. CMOS image sensor is important technology to include human eye function into mobile devices. RGB imaging in visible wavelength range (430 ~ 565 nm) can be disturbed by near infrared light (NIR, 700 nm ~ 1200 nm). In order to protect NIR light, we have developed NIR absorbing dye materials and its formulations composed of copper complexes, organic dyes, and binding polymers. Depending on ionic ligand types, absorption wavelength and solubility can be controlled. By adding coordinative ligands, absorption intensity and hydrothermal stability can be improved by John-Teller Distortion effect and binding energy, respectively. In this presentation, we will discuss about what is the failure origin to be stable under hydrothermal condition by analysis with XPS and FT-IR. Finally, designing photo-crosslinkable ligand without hydroxyl group, NIR absorbing Cu (II) phosphate/sulfonate materials will be presented.

4:15 PM EP11.02.03
Enhanced Surface Raman Laser with Organic Monolayer in Silica Hybrid Resonator Hyungwoo Choi, Xiaqin Shen and Andrea M. Armani; University of Southern California, Los Angeles, California, United States.
The performance and functionality of integrated optical devices are governed by their fundamental physical properties. In passive systems, such as waveguide arrays and interconnects, this limitation has pushed the field towards ultra-low loss materials that are compatible with conventional CMOS processing. However, this singular focus has resulted in a decrease in the functionality of these components and placed limitations on the ultimate system footprint. For example, one of the current drivers in the field is Si photonics. However, the refractive index of silicon places a fundamental minimum size in order to confine the optical mode. Similarly, due to its low second and third order optical nonlinear coefficients and high dispersion, it is challenging to achieve active components without high input power. By expanding the optical material toolbox, new strategies for designing optical devices and circuits will be possible. One emerging strategy for changing device performance is based on surface engineering. Originally focused on adding biologically active groups to a device for bio/chem detection, more recent work has explored developing passivating surface chemistries to stabilize or protect device surfaces. However, the majority of these efforts involved changing the device properties by adding material layers instead of directly changing the device material. In the present work, we develop and demonstrate an approach to directly change the Raman gain of the optical device by modifying the Raman of the dangling surface functional groups. The initial device studied as a proof of concept is an optical resonator; however, the basic strategy is suitable for any on-chip device. Optical resonators act as optical amplifiers, allowing low input powers to be significantly increased. One type of resonator is a traveling wave resonator or whispering gallery mode resonator. This cavity confines light in circular orbits, and due to photon storage times (or quality factors, Q) in the nanosecond regime, the input power can be amplified by over 100,000x. The large circulating optical intensities can reveal nonlinear phenomena that otherwise would require large pulsed laser systems. For example, previous work using silica cavities has demonstrated Raman lasing with only a few hundred micro-Watts of input power. However, the efficiency of the Raman generation was poor due to the intrinsically low Raman gain of silica.
In this present work, we fabricate silica resonators on chip. However, instead of relying on the intrinsic bulk Raman gain of the silica, we leverage surface chemistry to modify the disordered surface or boundary layer. As a result, a monolayer of oriented organic molecules is aligned with the circulating optical field in a microcavity. This optimization improves the light-matter interaction at the boundary layer, and the total Raman gain of the device. The two ordered monolayers studied are methylsilane (MS) and dimethylsilane (DMS). After attachment on the device surface, the devices still maintain ultra-high Q factors (over 10^7). Due to the alignment of the Raman modes of the siloxane molecule with the optical field, the efficiency and lasing thresholds are significantly improved. With an excitation source of 765 nm, low threshold SRS located at ~465 cm^{-1} is observed in both the MS and DMS functionalized devices with SRS efficiencies of approximately 40%. These efficiencies represent over 5 times enhancement as compared to bare silica devices. This work represents a new strategy for dramatically increasing the nonlinear optical performance of integrated photonic devices using organic molecules with a hybrid structure.

4:30 PM EP11.02.04
Thermally Soldered Au Nanogrids with Enhanced Plasmon Quality for Quantitative Multiplexing of Trace-Amount Molecules via SERS
Seunghee H. Cho and Yeon Sik Jung; Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daegon, Korea (the Republic of).

Trace-amount toxins in drinking water are not only serious environmental pollution but also threaten human health through long term accumulation. In need for sensors capable of detecting low-concentration, trace-amount molecules, highly sensitive and selective detection technologies have been long developed. Research has recently expanded to multiplexing, which can significantly reduce analysis time and sample volume while also providing a more thorough information of a given system such as that of the environment or a living cell. So far, multiplexing has largely been realized through assays based on highly sensitive fluorescent or electrochemical sensors, yet they lack in ability to differentiate from similar molecules and selectively recognize target molecules within mixed samples. Surface-enhanced Raman spectroscopy (SERS) has recently drawn much attention as a multiplexing technique owing to its fingerprint-spectra specificity and single-molecule level sensitivity. However, conventional approaches using lithography or metallic nanoparticles are either costly and time-consuming or show insufficient reproducibility. Recently, our group has demonstrated highly reproducible 3D cross-point Au nanostuctures for SERS based on high-resolution nanotransfer printing with uniform average enhancement factor of 4.1 × 10^4 over a macro-scale area. Herein, we present thermally soldered Au nanogrids with enhanced plasmon quality for highly sensitive detection of trace-amount molecules and accurate quantitative multiplexing via SERS. The Au nanogrids were fabricated by a thermal annealing method to solder multi-stacked 3D Au nanostucture into a single entity while preserving the sub-20 nm nanostructures. The enhanced plasmon qualities of Au nanogrids can be attributed to the reduced grain-boundary areas, enabling highly sensitive detection of low-concentration molecules through SERS. Au nanogrids were also functionalized with multiple single-stranded DNA (ssDNA) aptamer probes each specifically designed for different toxin molecules to achieve selective multiplexing and quantitative analysis. We used scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to characterize the nanostructure and grain morphology of Au nanogrids, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) to confirm aptamer-functionalization. As a result, we achieved three-component multiplexing and quantification of drinking water toxins each down to 10^{-11} M via SERS even without the use of Raman reporter dye-molecules.

4:45 PM EP11.02.05
High Performance Visible-Blind UV Photodetector Using ZnO@Au Core-Shell Nanostructures
Manjiri Singh1,2, Nisha Prakash1, Gaurav Kumar1,2, Suraj P. Khanna1,2, Prabir Pall1, Anil K. Thakur3 and Surinder P. Singh1,2; 1CSIR-National Physical Laboratory, New Delhi, India; 2AcSIR- Academy of Scientific & Innovative Research, CSIR-NPL Campus, New Delhi, India; 3Department of Nano Science and Materials, Central University of Jammu, Jammu, India.

Nanostructured materials with tailored geometries on the atomic scale having tuneable physico-chemical properties are of immense interest for applications in photodetectors. Among different reported nanostructured, metal nanoparticle on semiconductor nanowires has been proposed to improve performance parameters such as minimum dark current and enhanced UV performance of a photo-conducting device.1-3 However, the mentioned device geometries suffer from poor UV-to-Visible rejection ratio, as the top metal nanoparticle coating resists visible illumination.2 Therefore, we envisioned to develop the ZnO@Au core-shell nanostructures with metal (Au) core and semiconductor (ZnO) shell for photocductive device, to enhance UV emission1 detection as a result of SPR mediated carrier generation and transport with suppressed dark current. In present work, we have synthesized the ZnO nanostructures, without and with Au core, using wet chemical route. The ZnO and ZnO@Au nanostructures, were then deposited on ITO coated glass substrates followed by thermal annealing at 300 °C, under ambient conditions, forming ZnO/ITO and ZnO/Au) TIO nanostructures thin-film, respectively. Optical properties revealed that the incorporation of Au core in ZnO nanostructures reduces the overall optical bandgap of the material and also suppresses the visible emission originating from ZnO defect. Further, the electrical measurements shows suppressed dark current with enhanced light current under 380 nm UV illumination for ZnO/Au/ITO device, leading to 7 folds increase in photocurrent to dark current ratio (at 10 V applied bias) compared to the ZnO/ITO device. Additionally, the ZnO/Au/ITO device also demonstrates an improved UV-to-Visible rejection ratio (~1×10^{12}) compared to the ZnO/ITO device (~1×10^{10}) at 10 V applied bias and thus suggests its application in designing high performance Visible-blind UV photodetector.

References:

SESSION EP11.03: Cavity Quantum Electrodynamics
Session Chairs: Junichiro Kono and Xuedan Ma
Wednesday Morning, April 24, 2019
PCC North, 200 Level, Room 225 B

8:30 AM *EP11.03.01
Dressing Quantum Emitters with Nanoantennas and Microcavities
Vahid Sandoughdar; Max Planck Institute for the Science of Light, Erlangen, Germany.

Solid-state quantum emitters make up the most crucial components of any quantum information processing device. The quest for finding the ideal quantum system has led to a large effort on different materials, including organic molecules, semiconductor quantum dots, diamond color centers, rare earth ions in inorganic crystals and a variety of two-dimensional materials. While each system offers interesting features, the ideal system is still not within reach. One possible strategy to address this issue is, thus, to modify and improve the properties of the existing quantum emitters, e.g. by modifying their radiative decay rates and pathways using concepts from Cavity Quantum Electrodynamics. In our laboratory, we pursue this strategy and investigate the coupling of solid-state quantum emitters to microcavities and plasmonic nanoantennas.

In the first part of this presentation, I will discuss the room-temperature coupling of colloidal quantum dots to plasmonic nanostuctures. Semiconductor quantum dots are capable of emitting one, two or more photons after each excitation because of the possibility of generating multiple excitons within the same quantum dot. In practice, however, such multiphoton emission is often inefficient due to fast nonradiative decay channels such as Auger recombination. We have recently demonstrated that the biexciton emission efficiency can be significantly improved by a large radiative enhancement in the near field of a gold nanocone antenna fabricated by focused ion beam milling. We show that the quantum efficiency of the biexciton emission is increased by more than one order of magnitude to 70% in the coupled system. Moreover, by performing many quantitative in-situ measurements on the very same quantum dot, we demonstrate more than 100-fold radiative enhancement by the gold nanocone antenna for both excitonic and biexcitonic emission channels.

In the second part of my talk, I will show results on the cryogenic coupling of single organic molecules to open Fabry-Perot microcavities at the onset of strong coupling. Organic dye molecules are very strong emitters with near-unity quantum efficiency. However, their internal vibrational degrees of freedom and their coupling to the phononic landscape of their host matrix give rise to various sources of decoherence such that their use in quantum engineering becomes limited. To get around this effect, we couple an organic dye molecule to an ultrasmall Fabry-Perot cavity made of a curved (fabricated by focused ion beam milling) and a flat mirror. The ability to tune the cavity and scan it laterally across a thin molecular crystal allows us to perform several experiments with an exquisite control. Our results show that a dye molecule can be turned into a two-level quantum coherent...
system.

In closing, I discuss the prospects of hybrid quantum material based on plasmonic nanoantennas for use at room temperature.

9:00 AM • EP11.03.02
Manipulating Quantum Light on a Chip—From Heralded Single Photon Purification to Effective Photon-Photon Interactions Ronen Rapaport; Racah Institute of Physics and the Applied Physics Department, The Hebrew University of Jerusalem, Jerusalem, Israel.

Photons are a potential resource for a growing host of applications in quantum technologies and quantum information sciences. A particular interest is in effectively harvesting pure single photons from simple quantum emitters operating at room temperature, and in finding effective ways for strong interactions between only a few photons.

In this talk I will review our progress towards a realization of bright, high-purity single photon sources from impure photon emitters, by designing hybrid nano-emitter – nano-antenna devices that can efficiently extract and direct single photons using indeterministic two- photon states. I will also introduce our recent results showing on-chip low-loss guiding and large electrically-controlled enhancement of effective photon interactions in an optical waveguide by utilizing strong interactions of photons with dipolar excitations in semiconductors.

9:30 AM EP11.03.03
Path Selectivity, Lasing and Super-Radiance Effects in Plasmonic Nano-Structures—Experimental and Numerical Investigations Renaud Vallee1, Ibrahim Lounis2, Daniel Neuhauser3 and Serge Ravaine1; 1Centre de Recherche Paul Pascal, Pessac, France; 2LP2N, University of Bordeaux, Talence, France; 3University of California, Los Angeles, Los Angeles, California, United States.

Hybridisation of organic emitters and plasmonic nano-structures has attracted much attention over the last years, due to their interest in the design of plasmon-based nano-lasers [1,2] or to achieve long-range qubit entanglement [3,4]. Recent theoretical studies [5,6] suggest a plasmonic super-radiant mechanism to increase the rate of emitters, similar to Dicke super-radiance [7].

In this talk, we will report on the impact of plasmonic super-radiance and organic emitters close to a metal nanopore at room temperature. This observation of plasmonic super-radiance at room temperature opens questions about the robustness of these collective states against decoherence mechanisms which are of major interest for potential applications. A complete quantum theoretical/numerical approach will be presented, which will give full account of the obtained experimental results [8].

ii) We proposed a new type of nanodevice, capable of both path-selectivity and anisotropic lasing that is based on loss-compensation and amplification by a localized plasmon polariton [9]. The nano-device is a Y-shaped plasmonic nanostructure embedded in an anisotropic host medium with gain. The anisotropy leads to the path selectivity, an effect which is more pronounced once gain is included. The path-selectivity may be coupled with activation of a rotation of the anisotropic host medium for inducing a light-guiding switching functionality. On the experimental side, we used a DNA origami structure to precisely localize three different fluorescent dyes close to the tips of hollow gold nanotriangles. A spectral dependence of plasmon-enhanced fluorescence is evidenced through co-localized AFM and fluorescence measurements. The experimental results match well with explanatory FDTD simulations. Our findings open the way to the bottom-up fabrication of plasmonic routers operating through plasmon energy transfer. They will allow one to actively control the direction of light propagation [10].

References

9:45 AM EP11.03.04
Photonic Band Engineering in Absorbing Media for Spectrally-Selective Optoelectronic Films Botong Qiu, Yida Lin, Ebuka S. Arinze, Arlene Chiu, Lulin Li and Susanna M. Thon; Johns Hopkins University, Baltimore, Maryland, United States.

Spectrally-selective materials are of great interest for optoelectronic devices in which wavelength-selectivity of the photoactive material is necessary for applications such as multijunction solar cells, narrow-band photodetectors, transparent photovoltaics, and tailored emission sources. Achieving controlled transparency or opacity within multiple wavelength bands in the absorption, reflection, and transmission spectra is difficult to achieve in traditional semiconductors that typically absorb at all energies above their electronic band gap and is generally realized by the use of external bandpass filters. Here, we propose an alternate method for achieving spectral selectivity in optoelectronic thin films: the use of band engineering in 2D photonic crystal slabs within the absorbing region of a semiconductor in which resonant and confined photonic states are strongly coupled to the external reflecting and transmitting fields that share lateral wave-vectors.

As a first step, we use optical simulations to systematically study the effect of material absorption on the properties of the photonic bands in a slab-type photonic crystal structure. We find that adding weak loss, which is realized by introducing a small (~10%) imaginary part to the permittivity, does not appreciably change the frequencies of the photonic bands but does weaken the definition of the band structures. This is the result of reduced quality factors of the associated resonance modes due to the presence of dissipation. The results are also confirmed by qualitative analysis using perturbation theory. Critically, in the case where external propagating waves are incident upon or out-coupled from the photonic crystal slab structure, the radiating photonic bands induce multiple strong Fano resonance features in the slab transmission and reflection spectra, due to coupling between the bands and external fields. The Fano resonances display large transparency contrasts across the center of the resonances that should enable transmission and reflection wavelength selectivity and introducing material absorption into the model widens the bandwidth of this selectivity. Moreover, the absorption spectra also peak at these resonance frequencies, due to the associated concentrated field intensity inside the slab, with peak widths increasing under increasing dissipation, giving rise to the possibility of achieving spectral selectivity in the absorbing region of semiconductors.

We also demonstrate this tuning method experimentally by fabricating a proof-of-principle photonic structure consisting of a self-assembled polystyrene bead monolayer infiltrated with PbS CQDs that displays both near-infrared absorption enhancement and visible transparency enhancement over a homogeneous control film, qualitatively matching the bands and external fields. The Fano resonances display large transparency contrasts across the center of the resonances that should enable transmission and reflection wavelength selectivity and introducing material absorption into the model widens the bandwidth of this selectivity. Moreover, the absorption spectra also peak at these resonance frequencies, due to the associated concentrated field intensity inside the slab, with peak widths increasing under increasing dissipation, giving rise to the possibility of achieving spectral selectivity in the absorbing region of semiconductors.

In closing, I discuss the prospects of hybrid quantum material based on plasmonic nanoantennas for use at room temperature.

References

10:00 AM BREAK

10:30 AM • EP11.03.05
Diamond Quantum Photonics Constantin Dory and Jelena Vuckovic; Ginzioni Laboratory, Stanford University, Stanford, California, United States.

Optical quantum technologies will likely operate at the level of single or few photons. To guarantee high fidelity optical quantum computation and fast quantum communication rates, efficient, scalable, and versatile photonics is required. However, many promising material platforms, which host interesting quantum emitters, have challenging fabrication protocols. Moreover, to comply with the stringent fabrication constraints, traditional optimization methods are slow and device functionalities are limited.

Diamond hosts versatile color centers, some of which exhibit very long coherence times and/or minimal inhomogeneous broadening. Moreover, site-controlled implantation of color centers enables precise integration into on-chip optical circuits. To develop a diamond photonic platform that can match the scalability potential of the diamond color centers, major improvements in fabrication and device design are necessary. In our work, we have optimized fabrication methods based on quasi-isotropic etching and developed a
computational approach to inverse design photonics based on desired performance. Our design approach can include fabrication constraints as part of the optimization and thus results in robust designs. As our optimization methods can probe the entire parameter space our device designs are non-intuitive, but are fabricable using standard techniques, are robust against typical fabrication errors, and outperform state-of-the-art counterparts in footprint, efficiency and stability.

11:00 AM EP11.03.06
Photonic-Joined Structures—Microcavity Enhancement
Aziz D. Ruiz1,2 and Jorge A. Reyes-Esqueda1,2; 1UNAM, Mexico, Mexico; 2Instituto Física, UNAM, Coyoacan, Mexico; 1Postgrado Fisica Unam, Coyoacan, Mexico.

High light transmission microcavities are a greatly studied and applied topic [1, 2]. Lately, joined structures have drawn even more attention [3], like Fibonacci conjugated mirrors [4], because of its optical properties, as perfect transmission or field localization. Here, we study a simpler and novel joined structure, which presents high transmission (quasi-perfect for short arrays) in a resonant condition. In particular, we explore the transmission and field localization via simulations to manufacture the best arrangement in porous silicon: a Microcavity-3 Bragg Mirrors array. This is not a common microcavity, since it is composed by 3 Bragg mirrors, where the first two are in a symmetric configuration (microcavity), while the third one is in a conjugated configuration.

This sequence improves all the characteristics of common microcavities, particularly those for microcavities formed by absorbent materials.

References

11:15 AM EP11.03.07
Electron Transfer in Confined Electromagnetic Fields
Alexander Semenov2 and Abraham Nitzan1,2; 1Chemistry, the University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Chemistry, Tel Aviv University, Tel Aviv, Israel.

The interaction between molecular (atomic) electron(s) and the vacuum field of a reflective cavity generates a significant interest thanks to the rapid developments in nanophotonics. Such interaction which lies within the realm of cavity quantum electrodynamics can substantially affect transport properties of molecular systems [1-3]. For the last several years cavity-induced modifications of charge transport properties of molecular systems have drawn a considerable interest [4,5]. In our work we consider non-adiabatic electron transfer process in the presence of a cavity mode. We worked out a generalized framework of interaction between a charged molecular system and a quantized electromagnetic field of a cavity and applied it to the problem of electron transfer between a donor and an acceptor that are put in a confined vacuum electromagnetic field. The effective system Hamiltonian presents a unified Rabi and spin-boson model which includes a self-dipole energy term. This term which is usually neglected in the standard light-matter interaction models plays a crucial role in our formalism. Two limiting cases were considered: in the first case the electron is much faster than the cavity mode (slow mode) whereas in the second case the tunneling time of the electron is significantly larger than the period of the mode (fast mode). In the latter case the presence of the cavity does not alter the electron dynamics. In the case of slow mode, a Marcus-like electron transfer (ET) rate is obtained by summing over all final states and averaging over initial states of the electromagnetic field. We computed ET rates varying different system parameters. It was found that at high temperatures, high reorganization energies and/or low mode frequency the total rate can be described by a single Marcus rate with an increased reorganization energy whereas at low temperatures, low reorganization energy and/or high mode frequency the energy gap dependence of the rate exhibits local maxima which positions are defined by a resonance condition. Our study showed that a significant rate enhancement can be produced by the coupling to the field mode if the system is in the inverted region. The cavity-induced enhancement factor is larger at lower temperatures and/or at higher energy gaps. In the normal region the cavity-modified rate is smaller than the cavity-free one. The results of this work may offer a new way to control electron transfer. Using tunable highly-confined IR nanocavities one can easily manipulate the magnitude of ET rate by adjusting the mode volume or/and changing the relative orientation of the system with respect to the polarizability vector of the field. This opens new opportunities for manufacturing of nanodevices and stimulates new developments in infrared plasmonics.

References

11:30 AM *EP11.03.08
Nanoscale Self-Assembly to Smart Optical Materials
Yadong Yin; University of California, Riverside, Riverside, California, United States.

Smart nanostructured materials with optical properties responsive to external stimuli are gaining increasing interests due to their intriguing potential applications in printing, sensing, signage, security documents, displays, and other color-related devices. In this presentation, I will update our recent progress on the development of novel self-assembly approaches for the fabrication of various nanostructured materials whose optical properties can be dynamically tuned by controlling the spatial arrangement of the nanoscale building blocks. In particular, I will discuss the self-assembly of anisotropically shaped magnetic colloidal particles such as ellipsoids and cuboids into three-dimensional photonic crystals with strong field-direction-dependent diffraction. Then I will report the assembly and disassembly of plasmonic metal nanostructures and the associated opportunities in the development of novel optical devices such as humidity-responsive colorimetric sensors.

SESSION EP11.04: Excitons, Phonons and Polaritons
Session Chairs: Constantin Dory and Raktim Sarma
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 225 B

1:30 PM *EP11.04.01
Polaritons Beyond the Rotating Wave Approximation
Junichiro Kono; Electrical and Computer Engineering, William Marsh Rice University, Houston, Texas, United States.

Recent experiments have demonstrated that light and matter can mix together to an extreme degree, and previously uncharted regimes of light-matter interactions are currently being explored in a variety of settings, where new phenomena emerge through the breakdown of the rotating wave approximation [1]. This talk will summarize a series of
experiments we have performed in such regimes. We will first describe our observation of ultralong strong light-matter coupling in a two-dimensional electron gas in a high-Q terahertz cavity in a quantizing magnetic field, demonstrating a record-high cooperativity [2]. The electron cyclotron resonance peak exhibited splitting into the lower and upper polarization branches with a magnitude that is proportional to the square-root of the electron density, a hallmark of cooperative vacuum Rabi splitting, known asDicke cooperativity.

Additionally, we have obtained clear and definitive evidence for the vacuum Bloch-Siegert shift [3]. The second part of this talk will present microcavity exciton polaritons in a thin film of aligned carbon nanotubes [4] embedded in a Fabry-Perot cavity, also exhibiting cooperative ultralong light-matter coupling with unusual continuous controllability over the coupling strength through polarization rotation [5]. Finally, we have generalized the concept of Dicke cooperativity to a condensed matter system, demonstrating that it also occurs in a magnetic solid in the form of matter-matter interaction [6]. Specifically, the exchange interaction of N paramagnetic erbium(III) (Er3+) spins with an iron(II) (Fe2+) magnon field in erbium orthoferite (ErFeO3) exhibits a vacuum Rabi splitting whose magnitude is proportional to N\(^1/2\). Our results provide a route for understanding, controlling, and predicting novel phases of condensed matter using concepts and tools available in quantum optics, opening up a variety of exciting possibilities to combine the traditional disciplines of many-body condensed matter physics and cavity-based quantum optics.

References

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2:00 PM • EP11.04.02
Tunable Metamaterials for Vacuum Field Engineering of Two-Dimensional Systems
Jerome Faist; Institute of Quantum Electronics, ETH Zurich, Zurich, Switzerland.

When a collection of electronic excitations are strongly coupled to a single mode cavity, mixed light-matter excitations called polaritons are created. The situation is especially interesting when the strength of the light-matter coupling \(W_p\) is such that the coupling energy becomes close to the one of the bare matter resonance \(\omega_0\). For this value of parameters, the system enters the so-called ultra-strong coupling regime, in which a number of very interesting physical effects were predicted. Using metamaterial coupled to two-dimensional electron gases, we have demonstrated that a ratio \(\omega_0/W_p\) close to or above unity can be reached.

We also demonstrated that such ultra-strong light-matter coupling can be achieved using special geometries where the only less than 100 electrons are effectively coupled to the resonator. Other metamaterial engineering include the inter-meta-atoms coupling using a surface plasmon polariton resonance. This feature enables to restore the dispersion to the metamaterial ensemble and to control the linewidth of the latter. One very intriguing feature of ultra-strong light-matter coupled system is the prediction that photon pairs will be emitted through non-adiabatic modulation of the coupling. To this end, we have realized metamaterials based on high Tc superconductors that retain a high quality factor resonance for magnetic field up to \(9\) T and coupled them to two-dimensional electron gases. Because the resonator is designed to be switchable using the superconducting transition, experiment can now be conducted using very intense terahertz fields. We have also used transport to probe the ultra-strong light-matter coupling. As shown in Fig. 1, the longitudinal magneto-resistance of a two-dimensional electron gas is modulated by the irradiation by a weak, tunable THz source revealing the dispersion of the polariton branches. The effect of the vacuum field could be evidenced by a special metamaterial in which the vacuum field could be tuned by a mechanical plate brought in the vicinity of the resonator.


2:30 PM • EP11.04.03
Enhanced Light-Matter Interactions in Phononic Superlattices with Fine-Tuned Shape
Chun-Yu T. Huang1,2, Fariborz Kargar1, Bishwajit Deb Nath3, Topoji Deb Nath2, Adane Geremew2, Michael D. Valentin1,4, Ludwig Bartels1, Roger Lake1 and Alexander A. Balandin2; Phonon Optimized Engineered Materials (POEM) Center, Department of Electrical and Computer Engineering, Bourns College of Engineering, University of California, Riverside, Riverside, California, United States; 2Laboratory for Terascale and Terahertz Electronics (LATTE), Department of Electrical and Computer Engineering, University of California, Riverside, Riverside, California, United States; 3Materials Science and Engineering Program, University of California, Riverside, Riverside, California, United States; 4U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Similar to electron waves, the phonon states in semiconductors can undergo changes induced by external boundaries. The possibility of controlling the acoustic phonon spectrum in periodic structures has led to an explosive growth in the field of phononic crystals. A possibility of the acoustic phonon confinement effects in individual nanostructures has also been demonstrated experimentally [1]. The same periodic structures with properly tuned dimensions can act as phononic crystals affecting the light-matter interactions further. In this work, we conducted experimental and computational study to develop pillar structures, which act simultaneously as phononic and photonic crystals. The “pillar-with-hat” structures were fabricated using the electron beam lithography on a silicon (100) substrates, followed by the inductively-coupled plasma (ICP) cryogenic dry etching. The hats of the pillars were created with a special design to have exactly the same orientation plane as the substrate. The pillars, with the diameter and height of 280 nm and 362 nm, respectively, were positioned in the square array of 1×1 µm\(^2\) dimensions. We used Brillouin-Mandelstam light scattering spectroscopy as a tool to measure the dispersion of acoustic phonons with energies in the range from 0.5 GHz up to 900 GHz near the Brillouin zone center [2]. Changing the angle of light incidence with respect to the substrate allowed us to vary the probing phonon wave-vector, and determine the dispersion near the Brillouin zone center. We analyzed the contributions from all three mechanisms, which contribute to light scattering in our samples. They include scattering from the bulk, i.e. the volume of the substrate via the elasto-optic mechanism, from the surface of the substrate via the surface ripple mechanism, and from the side-facets of the pillars via the surface ripple mechanism. The finite-element modeling guided the nanostructure fabrication. We have found clear signatures of the phonon spectrum modification in the appearance of confined phonon sub-bands at the energies in the range from 2-20 GHz. The light reflectance has been strongly enhanced in certain directions. The experimental results confirmed the dual function of the structure as the phononic-photonic crystal. We argue that the dual function of the structure allows better control of the light-matter interactions, with important implications for engineering the radiative and non-radiative processes in the materials.

The work of the Balandin group was supported, in part, by the DARPA project W911NF18-1-0041 Phonon Engineered Materials for Fine-Tuning the G-R Center and Auger Recombination. Numerical simulations were supported in part by the NSF EFR-1433395. L.B. also acknowledges support from AFOSR under grant number FA9550-17-1-0377.


2:45 PM • EP11.04.04
Study of the Plasmon-Exciton Coupling in Hybrid Nanostructured Superlattices
Nicolas Large and Jose Luis Montaño-Priede; Department of Physics & Astronomy, The University of Texas at San Antonio, San Antonio, Texas, United States.

Plasmon-exciton coupling (plexciton) is a subject undergoing intense research to understand the electromagnetic interaction between plasmonic (metallic) and excitonic (semiconducting) materials and their promising applications in photonics. We investigate the extent on the plexciton (plasmon-exciton) coupling in a superlattice built with
periodically-distributed plasmonic cores with exitonic shells. We calculate the optical properties (extinction, transmittance, and reflectance) and the photonic band structure of micoscale cubic superlattice composed of 40-nm gold core (Au NPs) with 5 nm quantum shell (with exciton at 630 nm) arranged in a cubic array as a function of the inter-nanoparticles spacing (or lattice constant) from 5 to 35 nm. The photonic band structure of the smallest lattice constant present a band gap from 300 to 545 nm and a lower energy band density than those of large lattice constant in which the band gap disappears. The calculated extinction cross-section, transmittance, and reflectance show the plasmon-exciton coupling of the core-shell NPs and its decoupling as the distance between NPs increases. For these gaps, oscillations in their transmittance and reflectance appear as Bragg resonances above 600 nm wavelength. The resonance modes can be used to excite and enhance the interaction between the plasmons and the excitons.

3:00 PM BREAK

SESSION EP11.05: Metamaterials, Metasurfaces and Topological Photonics
Session Chairs: Peter Qiang Liu and Ronen Rapaport
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 225 B

3:30 PM *EP11.05.01
Topological Photonics via Parametric Driving Aashish Clerk; University of Chicago, Chicago, Illinois, United States.

Interest continues to grow in photonic and phononic analogues of topological electronic phases. These systems are typically non-interacting, and have the same band structure and edge state structure as their fermionic counterparts. In this talk, I’ll discuss recent theory work in my group on a class of photonic systems where this correspondence fails. They involve using parametric “two-photon” driving, and have Hamiltonians that superficially resemble those of topological superconductors. Among the surprising effects that emerge are the presence of topologically-protected instabilities that can be harnessed for non-reciprocal quantum amplification, and effective non-Hermitian dynamics in a bosonic analogue of the Kitaev-Majumdar chain. From an application point of view, parametric driving is an attractive route to topological photonics, as the generated gain inherently helps offset the impact of losses. I’ll discuss how our ideas could be realized in a variety of different experimental platforms.

4:00 PM *EP11.05.02
Hybrid Plasmonic and Dielectric Metasurfaces—From Optoelectronics to Nonlinear Optics Igal Brener and Raktim Sarma; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Metasurfaces, which are two-dimensional equivalent of metamaterials, offer a unique and efficient platform to study and control light-matter interactions in the sub-wavelength limit. When combined with semiconductor heterostructures, the metasurfaces can be coupled to fundamental excitations such as intersubband transitions in quantum wells. Such hybrid devices can provide opportunities for both fundamental studies of light-matter interactions as well as for new ultrathin optical devices such as voltage tunable optical modulators and nonlinear frequency generators. In the first part of this talk, I will present a low dissipation optical modulator using a hybrid plasmonic metasurface where the tuning mechanism relies on field induced tunneling of electrons in semiconductor heterostructures. In the second part of the talk, I will concentrate on hybrid dielectric metasurfaces that use using leaky mode resonances coupled to intersubband transitions for high efficiency and broadband second harmonic generation. I will finally conclude by presenting fundamental studies of strong-light matter interaction between Mie modes in dielectric resonators and intersubband transitions in semiconductor quantum wells.

4:30 PM...

Session Chairs: Peter Qiang Liu and Xue-Lan Ma
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

EP11.06.01
Detecting Visible Light by Solution Processed Oxide Absorption Layer for IGZO Phototransistor Jusung Chung, Won-Gi Kim and Byung Ha Kang; Yonsei University, Seoul, Korea (the Republic of).

Recently, many researches have been investigated on oxide semiconductor materials as alternative substance to silicon for various applications such as thin film transistor (TFT), photosensor, gas sensor, etc. It’s because they have superior electrical characteristics, compatibility with flexible substrates, high transparency, high field effect mobility, and low off-state current comparable to amorphous silicon. Among the applications, photosensor is attracting attention because it can be applied in various fields such as health care industry, intelligent display, and smartphone. However, the photosensor with oxide semiconductor has some issues that the wavelength range of the detectable light is limited due to its wide bandgap (>3 eV). Therefore, there are various studies about oxide semiconductor materials based photo transistors to detect visible light by stacking additional absorption layer composed of quantum dot, organic materials, and metal nanoparticle. However, they have disadvantages of high fabrication process, poor uniformity, and vulnerability to external environment.

In addition, some papers researched about the phototransistors with the only oxide semiconductor by controlling the sub-gap states in the oxide semiconductor to improve the light absorption characteristics in the visible light region (400-700 nm). They applied zinc tin oxide (ZTO) or indium zinc oxide (IZO) which have relatively higher oxygen related defects compared to indium gallium zinc oxide (IGZO). These oxide semiconductors act both channel layer and light absorption layer so that oxygen related defects could aggravate electrical characteristics and stability. By these problems, the phototransistor with oxide semiconductor cannot operate as photosensor device for a long time. Additionally, oxygen related defects mainly affect deep trap site, so the wavelength range of absorbable visible light by the oxide semiconductor is limited. Because of these factors, further studies are needed to absorb the entire range of visible light including red light. In this paper, we proposed indium-gallium-zinc-oxide (IGZO) phototransistors with...
simple fabrication process of stacking solution processed oxide light absorption layer (SAL). The phototransistor with the SAL was designed to have superior electrical and optical characteristics by separating the role of channel layer and light absorption layer. We generated sub-gap states in bandgap of SAL by low annealing temperature resulting in improved light absorption in visible light region (400 – 700 nm). The SAL was composed of IGZO which was similar with IGZO channel layer. The low annealing temperature process affect two type of defects, oxygen related defects and organic residue defects. The mechanism of visible light absorption by the SAL was verified by comparing the two type of defects, oxygen related defects and organic residue, and the results of optical characteristics of the phototransistor with the SAL. These sub-gap states caused SAL to absorb visible light despite the wide bandgap of IGZO (>3.0 eV). As a result, IGZO phototransistor with SAL has superior light absorption characteristics such as high photosensitivity of 127 A/W and photosensitivity of ~106 in red (635 nm) and green (532 nm) light region.

EP11.06.02
Robust Stretchable Photodetectors Based on Graphene/Co Heterostructure Shuchao Qin, Qianqian Du, Xinran Wang, Yongbing Xu, Yi Shi, Rong Zhang and Fengjie Wang; Nanjing University, Nanjing, China.

Graphene is being actively explored as a candidate material for flexible and stretchable photonic devices. However, the weak optical absorption of a monolayer carbon atoms and the absence of a gain mechanism have limited its responsivity. Here, we report a flexible photodetector with a high photosresponsivity and a fast response time from UV to visible range, using the graphene-Co all-carbon film on PET substrate, which is attributed to the efficient exciton dissociation at the graphene-Co interface and enhanced optical absorption of Co. In addition, the device exhibits good robustness against repetitive bending, suggesting its applicability in large-area array flexible photodetectors.

EP11.06.03
Improved Photovoltaic Performance of GaAs Solar Cells Enabled by Plasmonically Enhanced Spectral Upconversion Hyundong Chen1, Sung-Min Lee2, Angelo Montenegro3, Dongseok Kang3, Boju Gai4, Haneul Lim5, Chayan Dutta3, Wanting He3, Minjoo Lee3, Alexander Benderskii6 and Jongseung Youn4,5; 1Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2School of Materials Science and Engineering, Kookmin University, Seoul, Korea (the Republic of); 3Department of Chemistry, University of Southern California, Los Angeles, California, United States; 4Department of Electrical and Computer Engineering, University of Illinois at Urbana–Champaign, Champaign, Illinois, United States; 5School of Chemical Sciences and Environment, University of Illinois, Urbana-Champaign, Urbana, Illinois, United States; 6Department of Chemistry, Seoul National University, Seoul, Korea (the Republic of).

Spectral upconversion is a promising approach to circumvent the sub-bandgap transparency of single-junction solar cells by converting longer wavelength sunlight into high energy photons that can be readily absorbed. However, low intensity of one-sun illumination at relevant wavelengths of spectral upconversion inherently limits their practical application in photovoltaics. Here we present a composite module of GaAs solar cells that can provide meaningful enhancement of their one-sun photovoltaic performance by additionally capturing sub-bandgap photons via plasmonically enhanced spectral upconversion. Ultrathin GaAs solar cells with a specialized epilayer design are integrated on an upconversion medium containing NaYF4: Er3+, Yb3+ upconversion nanocrystals (UCNC), coated on a plasmonic reflector composed of hole-photonic hybrid silver nanostructure. The solar-to-electric conversion efficiency of GaAs solar cells on a UCNC-incorporated plasmonic substrate is improved by ~6.4% (relative) and ~11.8% (relative), respectively, compared to those on a nanostructured silver reflector without UCNC and on a plain silver reflector with UCNC, which is attributed to the combined effects of local electric-field amplification to enhance the absorption of UCNC, augmented upconverted emission via coupling into radiative modes, waveguided light concentration, as well as photon recycling.

EP11.06.04
Metal Nanoparticles on Crystalline Oxide Nanostructures for Surface Enhanced Raman Spectroscopy Bo Xiao; Norfolk State University, Norfolk, Virginia, United States.

We demonstrate a new paradigm for large-scale fabrication of metal nanoparticles on crystalline oxide nanostructures for surface enhanced Raman spectroscopy (SERS). A single-cell vapor-solid deposition was introduced to yield high-throughput SnO2 nanostructures with flexible control of size and geometry. Subsequent high-density Au nanoparticles with three-dimensional coverage on the oxide nanostructures were achieved through nucleation control in Volmer-Weber growth mode using physical vapor deposition at elevated temperatures. Au nanoparticles on SnO2 nanostructures operating in different “hot spot” modes exhibit the remarkable sensitivity of detecting trace concentrations molecules. This strategy also enables surface modification to alter hydrophilic to super-hydrophobic surfaces with contact angle over 150°. The manifestation of high-density metal nanoparticle formation presents a route to develop multifunctional nanostructures.

EP11.06.05
Tunable, Vivid Reflective Color Pixel Based on Active Fabry-Perot Broadband Absorber Soo-Jung Kim1, Heon Lee1 and Sung-Hoon Hong2; 1Korea University, Seoul, Korea (the Republic of); 2Electronics and Telecommunications Research Institute, Daejeon, Korea (the Republic of).

Structural colors based on Fabry-Perot (F-P) structure [1] has been received much attention in developing ink-free color painting for applications such as security devices, reflective display and functionalized color decoration. F-P absorbers have a simple structure thin metal-dielectric cavity- opaque thick metal without the need for complicated lithography process. F-P absorber can be fabricated over a large-area, and the reflective colors can be easily controlled according to the thickness of the dielectric layer for practical applications. However, asymmetric F-P cavities composed of bulk metal film exhibit an absorption spectra that has very narrow bandwidth, and it is difficult to achieve vivid color and wide color gamut in reflective color generation. [2] In previous other studies, the Cr and Ni lossy metals have been applied to F-P absorber instead of Ag and Au to widen the absorption band. But, a general metal deposition process such as sputtering or the vacuum evaporation has several drawbacks. One is that the physical properties of deposited metals are hardly controlled making it difficult to change the characteristics of the absorber. The other is that it is difficult to fabricate a large-area on various substrate because of high cost and time consuming.

In this study, we proposed a new active, vivid reflective color pixel based F-P cavity absorber using a lossy nanoporous material by the solution process. The nanoporous material made of chemically coupled silver nanocrystals (Ag NCs) with a conductive ligand, and this metal-dielectric composite film was applied to the top layer of the absorber to achieve a broadband absorption. Through finite-difference time-domain simulations and systematic experiments, we demonstrated that this combination generates enhanced color purity and provides an extended color gamut by controlling the dielectric cavity thickness. And, micro-size color pixel was actually actuated by incorporating a phase change material on F-P absorber.


EP11.06.06
Indium–Gallium–Zinc Oxide Based Visible Light Phototransistors Using Selenium Passivation Layer Hyukjoon Yoo, Won-Gi Kim, Byung Ha Kang, Hyoung Tae Kim and Hyun Jae Kim; Yonsei University, Seoul, Korea (the Republic of).

Recently, oxide semiconductors have attracted attention as new materials that can be widely used due to the outstanding characteristics of oxide semiconductor based devices, such as high mobility, low off current, and transparency compared to amorphous silicon based devices. Owing to these characteristics, oxide semiconductors are applied for a lot of electronic devices such as sensors and thin film transistors. In spite of this versatility, however, there is a limit to use oxide semiconductors as a phototransistor for detecting visible light region due to the high band gap energy (> 3 eV) of oxide semiconductors. Since the light of visible region has an energy of about 2 eV, the oxide semiconductor having high energy band gap cannot absorb the visible light. In order to overcome such disadvantages, researches have been conducted to fabricate visible light phototransistors by depositing a visible light absorption layer using quantum dots, nanowire, and 2D materials but there are problems such as complicated material synthesis process and difficulty in large area application.

In this study, indium–gallium–zinc oxide (IGZO) based visible light phototransistors were fabricated using a selenium passivation layer (Se PVL) as a visible light absorption layer. Selenium (Se) has photoconductive properties and exhibits conductive property only when light is irradiated. The Se PVL could be easily deposited by thermal evaporation process without any post treatment. It was confirmed that the IGZO phototransistors with Se PVL had the highest photoresponse characteristic at the Se PVL thickness of 150 nm. The IGZO phototransistors with Se PVL exhibited high photoelectronic characteristics such as photoresponsivity of 303.12 A/W, photosensitivity of 6.86 x 106, and detectivity of 60.
5.18 x 10⁻³⁴ Jones under 635 nm light illumination. Se showed the characteristics of p-type semiconductor and formed a large difference of valance band maximum in energy band alignment with IGZO layer. Therefore, electrons generated through absorption of visible light in Se PVL could be easily transferred to IGZO and affect electrical characteristics, while holes are not easily migrated due to valance band energy difference, so that recombination is prevented. The IGZO phototransistors with Se PVL exhibited excellent alignment with IGZO layer. Therefore, electrons generated through absorption of visible light in Se PVL could be easily transferred to IGZO and affect electrical characteristics, thereby creating patterned letters that emit different colors such as blue or green, from their backgrounds. Furthermore, the diffusion of dye molecules in the bleached region promoted a self-healing characteristic that could erase the patterned letters, which could enable the rewriting of different letters using the same PDMS. Using the proposed approach, we could pattern multi-color-emitting PDMS by taking advantage of the light-induced photobleaching phenomenon that is usually regarded as an undesirable effect in microscopy research. The introduction of this new way to realize rewritable, light-driven technology is highly meaningful because current approaches synthesize process. Using the conventional-dye-incorporated PDMS and photobleaching phenomenon for the reversible color changes would be an alternative approach to resolve the remaining challenges. We believe that this novel concept may find potential applications in many research fields, such as secure printing and optical storage devices.


EP11.06.07 Laser-Driven, Rewritable Writing Technology in a Full-Color Fluorescent Dye-Diffused Polydimethylsiloxane Elastomer Seongkyu Song and Soon Moon Jeong; Daegu Gyeongbuk Institute of Science and Technology, Daegu, Korea (the Republic of).

In this work, we present a new approach to demonstrate rewritable, light-driven recordings in polydimethylsiloxane (PDMS) by manipulating the light-induced photobleaching phenomenon [1]. The selectively photobleached red dyes turned transparent, thereby creating patterned letters that emit different colors such as blue or green, from their backgrounds. Furthermore, the diffusion of dye molecules in the bleached region promoted a self-healing characteristic that could erase the patterned letters, which could enable the rewriting of different letters using the same PDMS. Using the proposed approach, we could pattern multi-color-emitting PDMS by taking advantage of the light-induced photobleaching phenomenon that is usually regarded as an undesirable effect in microscopy research. The introduction of this new way to realize rewritable, light-driven technology is highly meaningful because current approaches synthesize process. Using the conventional-dye-incorporated PDMS and photobleaching phenomenon for the reversible color changes would be an alternative approach to resolve the remaining challenges. We believe that this novel concept may find potential applications in many research fields, such as secure printing and optical storage devices.

EP11.06.08 Absorption Enhancement of the Solar Spectrum with Arrays of Subwavelength Silicon Trumpet Non-Imaging Light Concentrators Ankit Chauhan1, Ashish Prajapati1, Dor Keizman1 and Gil Shalev2; 1Department of Electrical and Computer Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel; 2The Ilse-Katz Institute for Nanoscale Science & Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel.

Light trapping and the broad absorption of the solar radiation is important for photonic and nanophotonic applications ranging from sensing to harvesting of the solar energy. For example, appropriate light trapping supports the utilization of ultra-thin photovoltaic cells with enhanced efficiencies1-3. Efficient light trapping was demonstrated with surface arrays of subwavelength structures such as nanopillar (NP) arrays, nanocone arrays, etc4. In the current study we numerically explore light trapping based on surface arrays of subwavelength trumpet non-imaging light (NLC) concentrators (henceforth, trumpet arrays)5. Non-imaging optics was formulated in the regime of geometrical optics in the early 1970s. There are various members to the NLC family such as light cone (LC) NLC, paraboloidal NLC, conic paraboloid concentrators (CPC) and its derivatives, etc. The trumpet NLC (or hyperboloidal NLC) is an important NLC with an ideal concentration ratio as it accounts for both meridional rays as well as skew rays. We use finite-difference time-domain (FDTD) electromagnetic calculations to examine light trapping and broadband absorption of the solar radiation for laterally infinite cubic-tiled substrate-less silicon trumpet array under normal illumination. The absorptivity spectra of trumpet arrays are characterized by strong absorption peaks, some of which are just below the Yablonovitch limit, which is solely attributed to efficient occupation of the array Mie modes. We show that the absorption enhancement at the near infrared is an order of magnitude higher than that of optimized NP arrays. We show superior broadband absorption of the solar radiation in trumpet arrays (with unoptimized geometry) compared with that of optimized nanopillar arrays (~26% enhancement).

We show that low reflectivity is governed by modal excitations at the upper part of the trumpets (which is also supported by the weak dependence of the reflectivity on the array height), whereas the transmissivity is governed by modal excitation at the lower part of the trumpets. We show that the strong absorption peaks of trumpet arrays are governed by the interplay between reflectivity and transmissivity, and the corresponding excitations, which is tuned by adequate selection of the trumpet bottom diameter. The higher optical absorption in trumpet array is governed by low transmissivity, in contrast with nanopillar array in which the absorption is governed by low reflectivity.

References

EP11.06.10 Anthracene Dimers-Crosslinked Polyurethanes as Mechanoluminescent Polymeric Materials Lei Kan, Hao Wei and Ning Ma; Harbin Engineering University, Harbin, China.

Mechanoluminescent polymers have received arising attention in the research field of photovoltaic and material science in recent years. Anthracene compounds, which can photo-dimerize to form non-fluorescent dimers under 365 nm UV light irradiation and recover to the fluorescent monomers via heating or UV light of 254 nm, are good candidates of dynamic covalent systems for the research on mechanoluminescent polymeric materials. In this work, the anthracene dimers-crosslinked materials were pressed or scratched, indicating that the anthracene monomers were regenerated by mechanical attack chain scission of the dynamic dimer structure. 1H-NMR investigation confirmed the formation of anthracene monomers after the mechanical experiments and the process of the regeneration of the anthracene was simulated by finite element analysis. Furthermore, the average and total intensity of fluorescence increased with the increasing pressure applied on the PU materials, suggesting the formation of anthracene monomers was closely related to the external force. We hope that these anthracene dimers-crosslinked PU materials could provide a new avenue for fluorescent mechanosensitive materials. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)


Neutral transparent solar cells (TSCs) are highly desirable for building integrated photovoltaics and automobile applications. Transparency and photovoltaic conversion efficiency (PCE) have a trade-off relationship in the photovoltaics. Achieving high performance of TSCs while maintaining transparency is therefore extremely challenging. Here, we report the use of light absorption engineered Si microwire – transparent polymer composite films (SiMPF) as free-standing form to fabricate transparent hybrid solar cells with neutral color and high efficiencies. The controllable spacing between microwires enables to tune transparency of the devices. Moreover, the slanted SiMPF by a solvent-assisted wet etching exhibits excellent anti-reflection property while maintaining the transmittance of the devices compared to the flat ones. Finite-difference time-domain simulation reveals that the hemispherical losses are minimized and slanted SiMPF exhibited enhanced electric field distribution, encouraging the light-matter interaction. Finally, we apply p-type conductive polymer on the top and transparent conductive oxide on the bottom of the SiMPF, enabling us to fabricate neutral-colored semitransparent solar cells. Such devices demonstrate – 8% power conversion efficiency for visible transparencies of almost 10% retaining color-neutrality. These slanted SiMPF platforms are shown to have a significant advantage beyond the trade-off relationship between transparency and PCE, making them ideal TSCs.
Flexible Omnidirectional and Polarisation-Insensitive Broadband Light Absorber Weiling Dong1, Yun Cao2, Kuan Liu3 and Robert Simpson; 1Singapore University of Technology and Design, Singapore; 2Singapore; 3School of Optoelectronic Engineering and Instrumentation Science, Dalian University of Technology, Dalian, China.

Large-scale perfect light absorption in visible and near-infrared (VIS-NIR) spectrum are vital for efficient solar energy harvesting technologies. A wide range of metamaterial absorbers have been demonstrated, but they are limited by issues such as their high manufacturing cost, narrow band absorption, and incident angle sensitivity. We show a facile method to fabricate wafer-scale Ag-Sb2S3 nanoporous plasmon enhanced absorbers on plastic, crystalline and glassy substrates. This method is non-lithographic, and wet chemistry-free that exploits the immiscibility of Ag and Sb2S3 to control the surface morphology of the nanoporous structure[1]. Experimental results and numerical modelling show that the nanoporous structure has a high absorptance >80% over a wide spectral range from 300 to 2400 nm[1]. The high absorptance of the proposed Ag-Sb2S3 nanoporous structure is attributed to the excitation of Ag plasmon resonances and semiconductor bandgap absorption[1]. The high absorptance is independent of the polarisation state of the light and insensitive to the angle of incidence[1], which is a substantial advantage over many other metamaterial absorbers. We have also found that the Ag-Sb2S3 nanoporous structure is an effective absorber on both flexible and rigid substrates[1]. The simple room temperature co-sputter deposition method ensures that the Ag-Sb2S3 nanoporous structure can be grown on substrates such as flexible plastics, glass and ceramics, and other substrates at an industrial scale. In addition, these Ag-Sb2S3 plasmonic absorbers have other inter disciplinary applications including biosensing, which will also be introduced in this presentation[2].


Acknowledgements

This work was supported by Singapore China Joint Research Program (JRP) with grant number 2015DFG12630 from the International Science & Technology Cooperation Program of China and grant number 1420200046 from the Singapore Science & Engineering Research Council (SERC). T.C. acknowledges support from Program for Liaison Excellent Talents in University (Grant no. LQ2015021). W.D. is grateful for her SUTD President's Graduate Fellowship.

EP11.06.14

Significant Broadband Photocurrent Enhancement by Epsilon-Near-Zero Gold Nanostructures Photocathodes Shih-Hsuan Huang, Jian-Ming Chiu and Yian Tai; National Taiwan University of Science and Technology, Taipei, Taiwan.

The engineering of broadband absorbers to harvest white light in dye sensitized solar cells (DSSCs) is a major challenge in developing renewable materials for energy harvesting. In this study, gold (Au) rod-like sub-branches are successfully attached to the FTO substrate using an adhesive to produce the gold electrode. The proposed approach for fabricating photocathode is demonstrated to be facile and cost-effective, as opposed to existing techniques. Compared with electrodes prepared with sputtered Au, the Au rod-like sub-branches photocathode demonstrates significant increase of the power conversion efficiency (PCE) of a photoelectrochemical solar cell of 65% and higher catalytic activity with a cobalt-complex electrolyte. More importantly, the PCE of Au rod-like sub-branches photocathode improved by 16.6% compared to standard platinum (Pt) counter electrode. The increased efficiency is attributed to broadband absorption in the visible light region which due to incredible broadband plasmonic effect and presented lower lose in light-mater interaction of the Au. We have developed an electrochemical deposition process that enables scaled-up production of this nanostructures for large-scale energy-harvesting applications.

SESSION EP11.07: Light-Matter Interaction in Low-Dimensional Materials

Session Chairs: Andrea Alu and Antoine Reserbat-Plantey

Thursday Morning, April 25, 2019

PCC North, 200 Level, Room 225 B

8:30 AM *EP11.07.01

Control of Light-Matter Interaction in van der Waals Materials Vinod Menon; Physics, City College & Grad Center of CUNY, New York, New York, United States.

Two-dimensional (2D) van der Waals materials have emerged as a very attractive class of optoelectronic material due to the unprecedented strength in its interaction with light. In this talk I will discuss approaches to control this interaction by integrating the 2D materials with microcavities, and metamaterials. I will first discuss the formation of strongly coupled half-light half-matter quasiparticles (microcavity exciton-polaritons) in the 2D transition metal dichalcogenide (TMD) systems and approaches to optically/electrically control them [1-3]. The possibility to enhance the nonlinear optical response of the polariton states by exploiting the higher order Rydberg states in TMDs will also be discussed. We will also present our recent work on chiral metasurfaces to address and route the valley excitons in 2D TMDs. Finally, we will discuss the realization of room temperature quantum emitter array using strain engineered hexagonal boron nitride [4] and coupling them to high quality factor resonators.


9:00 AM *EP11.07.02


The isolation of stable atomically thin two-dimensional (2D) materials on arbitrary substrates has led to a revolution in solid state physics and semiconductor device research over the past decade. 1 A variety of other 2D materials (including semiconductors) with varying properties have been isolated raising the prospects for devices assembled by van der Waals forces. 2 A fundamental challenge in using 2D materials for optoelectronic devices is enhancing their interaction with light, ultimately responsible for higher performance and efficiency in the devices. In particular, for photovoltaics; inorganic materials (e.g., Si, GaAs and GaInP) can concurrently maximize absorption and carrier collection. But thin film absorbers have lacked the above ability due to surface and interface recombination effects. In contrast, Van der Waals semiconductors have naturally passed surfaces with electronically active edges that allows retention of high electronic quality down-to the atomically thin limit. In this seminar, I will show our recent work on photovoltaic devices from transition metal dichalcogenides of molybdenum and tungsten such as MoS2, WSe2 etc. We have recently demonstrated near-unity absorption in the visible part of the electromagnetic spectrum in < 15 nm films of these semiconductors by placing them on reflecting metal substrates such as gold and silver. We have further shown that these highly absorbing, ultrathin films can be further used for fabrication of simple Schottky junction photovoltaic devices with microfabricated metallic top contacts. 3 While, this work helps solve the light-absorption problem, the external quantum efficiency EQE was < 10% for our Schottky junction devices. Very recently, we have extended this early work to fabricate p-n heterojunctions from p-WSe2/n-MoS2 and use graphene as a transparent top contact to amplify our current collection efficiency and push the EQE up to 50%, 4 approaching that of many emerging photovoltaic technologies with active layers in the 100s of nm range. This represents a significant development as both light-absorption and charge collection have been addressed in these devices.


9:30 AM EP11.07.03

Extraordinary Light Absorption and Photoluminescence of Graphene Nanostripes Deepan Kishore Kumar2, Jacob Bagley3, Wei-Shiuan Tseng4, Dorte R. Danielsen1 and Nai-
Graphene has gained enormous research interest over the past two decades due to its unique electronic and optical properties. A single atomic layer of carbon atoms with the honeycomb structure has a universal optical absorption around \(\alpha \approx 2.3\%\), which is defined by the fine structure constant \(\alpha\). This is scientifically unprecedented for materials, but is too small for useful optoelectronic applications. Here we report the production of nearly perfectly light absorbing graphene nanostripes (GNSPs) from a single-step, high-yield, plasma enhanced chemical vapor deposition (PECVD) method using an aromatic precursor (Dichlorobenzene) that enables vertical growth of graphene nanostripes on substrates. The quality of the GNSPs was evaluated using Raman spectroscopy, EDS and XPS techniques to confirm the absence of any dopant, and UPS measurements of the work function at \(\approx 4.45\) eV further confirmed the purity of GNSPs was comparable to pristine graphene. The optical absorption spectra of vertically grown GNSPs revealed nearly perfect absorption over the visible spectral range from 400 nm to 900 nm. The mechanism for nearly complete light absorption may be understood from the gapless nature of graphene that can absorb all wavelengths through carrier excitations and the presence of multiple internal light scattering mechanisms of GNSPs that are stacked in a turbostratic fashion (i.e., rotationally disordered). To investigate whether GNSPs, being a good light absorber, may also be a good light emitter, we investigated the photoluminescence (PL) of GNSPs using a confocal laser scanning Light Sheet Microscope (LSM 880). GNSPs were transferred from the growth copper substrates by either mechanical exfoliation onto a glass substrate or liquid phase exfoliation using N-methyl-pyrrolidone (NMP). We observed a broadband nonlinear emission in the visible spectral range for continuous wave (CW) laser excitation wavelengths at 405nm, 450nm, 488nm, 514nm, 561nm, 589nm and 633nm. The nonlinear nature of emission was manifested by the experimental observation of a blue shifted emission tail above the energy of the excitation laser. Under the same laser power, the emission spectrum was found to redshift with decreasing laser excitation energy, and the emission intensity also decreased substantially with decreasing laser excitation energy, showing ~5 times weaker emission intensity for excitation wavelength at 633nm relative to that for excitation wavelength at 405nm. While emission for a given laser excitation energy only appeared above a threshold laser power, strong light emission was already observed for laser powers as low as ~0.03mW, which was much stronger than most conventional fluorophores. These preliminary findings suggest that the mechanism of light emission may be qualitatively attributed to thermal emission of hot electrons that interacted with strongly coupled optical phonons (SCOP) and topological defects (e.g., the Stone–Wales defects as confirmed by TEM and AFM) in GNSPs, although more systematic and quantitative studies are still necessary to elucidate the underlying physics. All in all, the extraordinary light absorption and photoluminescence found in PECVD-grown GNSPs suggest that GNSPs are promising for use as an active layer in high efficiency photovoltaic devices and tunable light emitting devices.

9:45 AM BREAK

10:15 AM *EP11.07.04 Plasmonics over Hybrid Metasurfaces Siyuan Dai1, Alex Krasnok1 and Andrea Alu1,2; 1City University of New York, New York, New York, United States; 2The University of Texas at Austin, Austin, Texas, United States.

In this talk we discuss our recent effort in the context of hybrid metasurfaces formed through nanophotonic engineering metasurfaces and 2D materials, reporting our recent theoretical and experimental results in the context of hyperbolic plasmon propagation and embedded eigenstates. During the talk we will discuss their highly unusual light-matter interactions and potential opportunities for nanophotonic devices.

10:45 AM *EP11.07.05 Active Control of Single Photon Sources Using 2D Materials Frank Koppons and Antoine Reserbat-Plantey; ICFO - The Institute of Photonic Sciences, Castelldefels, Spain.

Solid state quantum emitters are a mainstay of quantum nanophotonics as integrated single photon sources (SPS) and optical nanoprobes[1,2]. Integrating such emitters with active nanophotonic elements is desirable in order to attain efficient control of their optical properties but typically degrades the photostability of the emitter itself[2]. In our group, we have developed optomechanical[3] and optoelectrical[4] approaches to either tune energy and decay rate of single photon sources. In this talk, I will present recent experiments[4] that demonstrate a tuneable hybrid device which integrates lifetime-limited single emitters (linewidth 40 MHz) and 2D materials at sub-wavelength separation without degradation of the emission properties. Our device’s nanoscale dimensions enable ultra-broadband tuning (tuning range > 400 GHz) and fast modulation (frequency 100 MHz) of the emission energy, which renders it an integrated, ultra-compact tuneable SPS. Conversely, this offers a novel approach to optical sensing of 2D material properties using a single emitter as a nanoprobe, present a new type of hybrid system, consisting of an on-chip graphene SNSs suspended a few tens of nanometres above nitrogen-vacancy centres (NVCs), which are stable single-photon emitters embedded in nanodiamonds.

References

11:15 AM EP11.07.06 Plasmon Induced Thermoelectric Effect in Graphene Viktoria Shautsova1,2, Themistoklis Sidiropoulos2,3, Xiaofei Xiao2, Nicholas Güsten3, Nicola Black2,4, Adam Gilbertson2, Stefan Maier2,4, Lesley Cohen2 and Rupert F. Oulton2; 1University of Oxford, Oxford, United Kingdom; 2Imperial College London, London, United Kingdom; 3ICFO–The Institute of Photonic Sciences, Barcelona, Spain; 4National Physical Laboratory, London, United Kingdom; 5Nanoinstitut München, Munich, Germany.

While graphene is a promising material for novel photonic devices due to its broadband optical absorption, ultrafast carrier dynamics and electrical tunability [1], the quantum efficiency of graphene devices is intrinsically limited by low absorption of graphene (2.3% of normal incident light). To enhance light-matter interaction, optical focusing elements such as plasmonic metal nanoparticles (NP) can be utilized [2]. Here, we report our recent results on the graphene plasmonic NP hybrid structures. Femtosecond pump–probe measurements of graphene nearby plasmonic gold nano-disc structures confirm the presence of a strong near-field interaction leading to hot carrier generation in the graphene; however, the results suggest that the hot carriers arise dominantly from direct photoexcitation in the graphene with a minimal contribution from charge transfer from the gold [3]. Next, asymmetric plasmon-nanobar electrical contacts are employed with a view to create an electronic temperature gradient across a homogeneous graphene channel, which results in photothermal electricity (PTE) current generation [4]. At certain conditions, the plasmon-induced PTE photocurrent can be directly isolated. In this regime, the device effectively operates as a sensitive electronic thermometer providing access to plasmon induced local carrier temperature which is estimated to be of the order of 2000 K. These results are of particular importance for development of hot carrier based plasmonic devices.

[2] Z. Fang et al. Nanolett 12, 3808 (2012);

11:30 AM EP11.07.07 Anomalous Second Harmonic Generation in Monolayer Molybdenum Disulfide Brian Squires, Yuri Rostovtsev and Arup Neogi; University of North Texas, Denton, Texas, United States.

The second order nonlinear optical process of second harmonic generation should theoretically scale quadratically with respect to input power. Deviations from this exponent can be used as a tool to characterize dissipative and coherent processes at the micro scale. We use this new methodology to characterize dissipative processes in monolayer MoS2, which can be attributed to two-photon-absorption, free carrier absorption, and phonon related processes. Additionally, we observe a significantly reduced second harmonic generation power factor for CVD grown MoS2 on GaN which we attribute to efficient electron-phonon coupling due to lattice-matched interface phonons, indicating enhanced thermal dissipation at the boundary. When pumped below the band gap but close to two photon resonance to the C-exciton band, we observe a substantially enhanced second harmonic generation power factor which we explain via a quasi-two-state superradiance model. A singularity in the density of states in MoS2 arises at the C-exciton energy due to
Enhancement exceeding the theoretical double-pass absorption (J<sub>p</sub>) of state-of-the-art efficiency of 19.9%. A detailed loss analysis is conducted and provides a pathway for reaching 25% conversion efficiency in ultra-thin GaAs solar cells using the same light-capturing and conversion mechanisms.

Flexible and Reconfigurable Plasmonics

Over the past decade, significant progress in controlling light-matter interactions at the nanoscale has been achieved. Most of the advances, however, have relied on static systems limited to the as-fabricated or as-synthesized metal nanostructures. This talk will discuss how the ability to tune plasmonics responses reversibly may address key challenges in future nanoscale optics. We will highlight how the fabrication and scalability of responsive nano-optical substrates can be used in diverse applications from stretchable nano-lasing to reconfigurable sensing and imaging.

Light Trapping in Nanowires for Photovoltaic Applications

Optical absorption in nanowire arrays is intensively explored to enhance performance of photovoltaic devices. At normal incident light, vertically standing nanowires act as optical nano-antennas and show up resonant optical modes in their absorption spectra at special wavelengths due to their comparable dimensions to optical wavelengths. To achieve high performance photovoltaic devices, near-unity absorption spectra of nanowires are necessary and are gained through optimizing geometrical parameters of the nanowires [1]. Conventionally, longer nanowires or denser arrays of nanowires (smaller pitch) are used to approach near-unity absorption of the excited optical modes at the expense of larger material volume of nanowires. However, employing light trapping mechanisms in nanowires are the alternatives to enhance absorption of the excited optical modes without increasing the material volume [2], reducing the total cost. The light trapping through increasing optical path length of the optical modes improves absorption of an excited optical mode in constant material volume, enhancing absorption efficiency due to both reducing light reflection at the interface of air/nanowires, and reducing light transmission at the interface of nanowires/substrate. In this study, we improved the effective near-unity absorption spectra in nanowires, we take advantage of light trapping mechanisms in nanowires through embedding distributed Bragg reflectors (DBRs) in the bottom as well as in the top part of InP nanowires, respectively. Our calculations show that by employing the DBRs of only two periods of InGaAs/InP, an unselective absorption spectrum is obtained at normal incidence. At the presence of oblique light incidence, the integration absorption efficiency enhances up to about 85% at 50° compared to 79% at normal incidence. Increasing the period number of the DBRs from two to five, this value increases even upper to about 95% [3]. The improvement is due to decreasing light transmission of the excited optical modes from the nanowires into the substrate. The results are expected to be valid for other direct bandgap III-V semiconductor materials. Taking advantage of DBRs to enhance optical absorption in nanowires offers a great potential for novel high-performance photovoltaic applications.

Quantum Dots: For High-Efficiency Solar Cells

Quantum dot antennas have potential to increase the light trapping efficiency and concentration factor for planar luminescent solar concentrators. We report here on quantum dot antennas designed for a fabricated tandem luminescent solar concentrator (LSC) that consists of a Si bottom cell and a top cell LSC with highly efficient CdSe/CdS quantum dot (QD) isotropic lumineshores evenly dispersed in a poly(laurylmetacylate) (PLMA) waveguide, optically coupled to a micro-array of InGaP top cells. The QDs absorb light in in 300-500 nm wavelength range and emit luminiscence radiation at 653 nm, a wavelength matching the band edge of the InGaP cells. In previous LSC top cell designs, wavelength-selective mirrors have been used to spectrally reflect and trap the radiated QD emission within the waveguide. We compare the light trapping and concentration factor for planar waveguide designs employing Bragg filter top mirrors and metasurface bottom mirrors with quantum dot antennas. Metasurface mirrors are formed from a high index (n>3) material patterned as a hexagonal array of cylindrical pillars of subwavelength thickness onto a glass (n≈1.5) substrate. This LSC is integrated with a Si bottom cell to form a 4 terminal tandem with a maximum theoretical efficiency of 29.4% with a projected tandem module cost of $8130/m². A limiting factor in current LSC design is related to the tandem efficiency of the QDs. The radiated emission can be lost through the escape cone or be parasitically lost within the waveguide. By forming quantum dot antennas, consisting of QDs coupled directly to the pillars of the metasurface bottom mirror, we can induce highly directional, oblique anisotropic QD emission, reducing escape cone losses, and thus potentially eliminating the need for a spectrally-selective top mirror. We simulate quantum dot antennas composed of aluminum antimonide, silicon, and silicon carbide and find a maximum achievable efficiency of 32.2% with a lower projected tandem module cost of $6387/m².
Nanosized structures introduce new ways for manipulating light injection, coupling and trapping at the subwavelength scale. A number of nanoscale light trapping structures that can efficiently control and enhance light absorption have been reported such as, inverted nanoprisms, nanowires, quasi-random patterns, and nanocones, mainly focusing in the optical domain, with very few modifications. The famous nano-structure in this study area is known as “black silicon” exhibiting nearly zero reflection over a broad solar spectrum range. The complexity of these structures comes when are integrated into real devices. The challenging problem is not to compromise the optical enhanced character of silicon by the electrical losses such as the recombination at the solar cell surfaces. Since black silicon devices exhibit large surface areas, minimising surface recombination is mainly difficult. There are reports on high efficient black silicon solar cells thus far have yet not been able to compete with conventional silicon devices. Jibun and the co-workers have reported an 18.2% efficient all back contact (ABC) black silicon device$^6$. They find that the dominant recombination process can be reduced by careful monitoring of the doping profile of the structured surface. They report that efficiency limitation is mainly due to Auger recombination whereas surface recombination only dominates at low doping density profiles. In contrast, Hele Sevin et al. report a 22.1% black silicon IBC device by passivating the surface recombination through the deposition of a conformal layer of alumina$^7$.

Here, we demonstrate the fabrication of quasi-random nanophotonic structures that have similar optical properties as black silicon and integrate them by both wet and dry processing. We also fabricate state-of-the-art light trapping structure, micron-sized pyramids and realize into silicon solar cell. We present a quantitative comparison of these nanophotonic structures both in the electrical and optical domain, evaluating the impact of plasma dry etching by comparing the same nanostructures made of wet chemical etching. Furthermore, it is an interesting study to understand whether the taper walls of the wet etched structure improves the antireflective (AR) property compared to the vertical walls realized by dry etching. Ultimately, we also show a detailed comparative study of micro vs nano, structures to address the question of whether nanostructuring to improve the optical performance of solar cell devices without compromising their electrical efficiency.

Here, a thermionic power converter fabricated from gold nanostructures is systematically tested. Periodic patterned gold nanostructures are fabricated through electron beam lithography. With laser excitation at different incident power and wavelength, the corresponding thermionic emission current is collected at a paired ITO anode. Short circuit current \( J_s \) and open circuit voltage \( V_{oc} \) provide a unique way to pinpoint the effective electronic temperature of the ‘hot electron’ distribution as well as its relative population compared to thermalized electrons. The wavelength and geometry dependence study reveal detailed insight into the light-matter interaction and electron-phonon coupling dynamics. Additionally, the experimentally observed electronic temperature of the non-thermal electron gas is also supported by anti-Stokes Raman thermometry recently developed in our group.

Nanoscale assembly coupled with competing anisotropic interactions can produce complex structures and provide additional degrees of freedom for tailoring their collective properties. However, the ongoing researches are highly limited by the poor quality of building blocks, inaccessibility of direct observation of crystal structures and lack of reliable numerical methods for analyzing their dynamic anisotropic interactions. In this presentation, we report magnetic assembly of super uniform magnetic nanorods into responsive body-centered tetragonal (hct) photonic crystals. The assembled structures are fixed during assembly by silica coating and directly characterized under electron microscopy, which suggests a body-centered tetragonal (hct) crystal structure. Finite-element calculations show that two magnetic nanorods approach thermodynamic equilibrium when the tangent components (orthogonal to the surface normal) of their magnetic forces is zero, showing good agreement with structures from TEM images of the assembled crystals. This method provides reliable analytical approach towards understanding the anisotropic interactions between building blocks. Thanks to the pretty good orders of the crystals, well-defined diffraction peaks are observed during SAXS measurements, which is consistent with the hct structures obtained by TEM images and provides detailed information about assembly kinetics. In combination with high packing density, the assembled photonic crystals exhibit extremely bright structural colors, whose intensity overwhelms our other tunable photonic crystals. In addition, the diffraction peaks and structural colors can be continuously tuned across visible range by varying the directions of magnetic field. We also extend the assembly strategy to other morphologies, like nanocubes and nanoplates. In the case of nanocubes, they tend to assemble along \([110]\) direction (edge to edge) as determined by the interplay of the shape and magnetic anisotropic interactions. In case of nanoplates, however, 2D photonic crystals are more favorable due to the symmetry breaking along the directions orthogonal to assembly axis (direction of external magnetic fields).

Anisotropically Shaped Cu Nanostructures as Emerging Plasmonic Materials

Jiansen Chen\(^1\), 2 and Yadong Yin\(^1\); 1University of California, Riverside, Riverside, California, United States; 2Soochow University, Suzhou, China.

Plasmonic materials have been extensively studied because of their broad applications in areas such as chemical and biological sensing, bioimaging, and solar energy conversion. So far major research efforts have been limited to noble metals particularly gold and silver due to their considerably large scattering and absorbance cross-sections as well as high chemical stability. However, these noble metals have limited earth abundance, making their large scale application impossible. Although much desired, little progress has been made to the development of non-noble-metal-based plasmonic materials due to their weak plasmonic response and/or low chemical stability against oxidation. In this presentation, we first analyze theoretically the plasmonic characteristics of copper using FDTD solution, and demonstrate that copper nanostructures can be made highly active in surface plasmon resonance if their resonance mode can be shifted to infrared to avoid the overlap with the intrinsic interband transition. Practically, this can be achieved by adopting an anisotropic shape such as plate and rod. The challenge however is the synthesis of copper nanostructures with well-defined anisotropic shapes using wet chemical approaches. In the second part of the present work, we report a seed-mediated templating growth method for the preparation of copper nanorods with highly controllable dimension and excellent size/shape uniformity. The resulting copper nanorods show surface plasmon resonance in infrared with intensity comparable to or better than silver and gold counterparts. With the protection of a crosslinked polymer layer, the nanorods also display considerably high stability against oxidation. Lastly, by taking advantage of their excellent photothermal conversion efficiency and high stability, we integrate the copper nanorods into the fabrication of shape-memory polymer nanocomposite and further demonstrate the construction of smart microrobots whose mechanical movement can be fully controlled by the illumination of light.
optical simulations, we show that these supercrystals exhibit Mie resonances both in scattering and absorption. This photonic behavior leads to absorption efficiencies of QD supercrystals greater than unity in a wide spectral range in the visible. Finally, we investigate QD coupling in supercrystals via ultrafast spectroscopy, finding that QD supercrystals feature a transition from bound to free biexciton as the interparticle distance decreases.

Plasmonic perfect absorbers can exhibit nearly 100% absorptivity at desired wavelengths, and also emit light at the same wavelengths when they are heated. It has been successfully demonstrated their use such as in wavelength-selective infrared thermal emitters and molecular vibrational sensors. In this seminar I will summarize some recent studies in our group on the perfect absorbers based on the metal-insulator-metal structures, Fabri Perot or other similar types of cavity structures as well as 2D patterned structures. Some of the fabricated mid-infrared perfect absorbers exhibit narrowband resonant absorption as narrow as 22 nm with efficiency higher than 97 %. We introduce some applications of these devices such as for selective thermal emitters operated above 1273K, selective surface-enhanced vibrational spectroscopy for high-sensitivity molecular sensing, and wavelength selective IR detectors in combination with pyroelectric, thermoelastic, and bolometer devices.

**SYMPOSIUM EP12**

**Emerging Materials for Plasmonics, Metamaterials and Metasurfaces**  
April 23 - April 25, 2019

**Symposium Organizers**  
Viktoria Babicheva, The University of Arizona  
Kuo-Ping Chen, National Chiao Tung University  
Marina Leite, University of Maryland  
P. James Schuck, Columbia University

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* Invited Paper

**SESSION EP12.01: Nano-Optics**  
Session Chairs: Viktoria Babicheva and Marina Leite  
Tuesday Morning, April 23, 2019  
PCC North, 200 Level, Room 226 A

**11:00 AM EP12.01.01**  
**Polarization Manipulation via Surface Phonon Polariton Nano-Resonators**  

The polarization of light is of interest in several technologically relevant fields ranging from chemical identification, where the differing handedness of a molecule can drastically alter its effects on the human body, to quantum computing, with the polarization of light serving as a qubit. Here, we report the polarization properties of L-shaped localized surface phonon polariton resonators etched into 6H-SiC, with modal Q-factors as high as 144. These high Q-factors allow us to identify three resonances and observe their evolution as a function of asymmetry, which would otherwise be muddled by the loss-induced broad linewidths in the comparable plasmonic structures. Full-wave electromagnetic simulations of the resonator reflection spectra and resonant charge distribution indicate that the low- and mid- energy modes are characterized by a longitudinal dipole and transverse dipole, respectively. This behavior is corroborated by polarization dependent reflectance measurements and simulations that reveal orthogonal excitation axes for these two modes for the symmetrical resonator. However, this orthogonality is broken as the relative leg length is increased. Interestingly, the simulated resonant charge distribution of the high-energy resonance suggests that it is associated with a higher order longitudinal mode. However, unlike the longitudinal dipole mode, the higher-order mode exhibits an anomalous polarization dependence that is characterized by a spectral weight that is only weakly dependent on the incident polarization. Furthermore, as this higher energy mode is tuned into resonance with the normally IR inactive zone folded longitudinal optical phonons, a coupling behavior is observed between the surface phonon polariton mode and the bulk phonons, with the resonant intensity of the phonon modes following the polarization dependence of the higher energy mode.

**11:15 AM EP12.01.02**  
**Photonic Materials for Solar Sail Interstellar Missions**  
Artur R. Davoyan; University of California, Los Angeles, Pasadena, California, United States.

We discuss photonic material and design challenges facing future solar sail based interstellar missions. We discuss extreme conditions of solar radiation and corona that sails are exposed to during a solar gravity assist phase and outline designs that enable sustainable sail designs. At present deep space exploration is limited by transit time and overall mission costs. Conventional space transportation systems typically employ chemical or solar electric propulsion, which have effectively reached the limit of their maximum performance potential; further development activities focus mainly on improving reliability and reducing cost. Recent studies show that solar sails with high area-to-mass ratios and less than 0.1 AU perihelion approach (i.e., <20 solar radii) may enable missions with >30 AU/year propulsion, which have effectively reached the limit of their maximum performance potential; further development activities focus mainly on improving reliability and reducing cost. We show that with a proper photonic design polar resonances of the aforementioned materials may harnessed to obtain relatively large emissivity and achieve sustainable sail propulsion, which have effectively reached the limit of their maximum performance potential; further development activities focus mainly on improving reliability and reducing cost.

Next, we consider photonic designs that optimize reflectance and hence the radiation pressure force. We highlight the mass – reflectance tradeoff and show that sail materials with >20 AU/year are feasible. We show that conventional polymer based sails cannot withstand high solar flux and justify the need for novel sail materials. We discuss necessary criteria and show that sails based missions necessitate a very close pass near the sun, where the sail is exposed to extreme conditions of solar radiation and corona. Here, we study photonic properties of sail materials and discuss criteria needed for the design of such extreme solar sails.

Finally, with radiative cooling being the sole mechanism for thermal management, we study nanopatterning of the sail materials to increase their thermal emissivity in the infrared. We show that with a proper photonic design solar resonances of the aforementioned materials may harnessed to obtain relatively large emissivity and achieve sustainable sail temperatures, below the melting point of its constituent materials.

**SESSION EP12.02: Emerging Phenomena**  
Session Chairs: Viktoria Babicheva and Artur Davoyan  
Tuesday Afternoon, April 23, 2019  
PCC North, 200 Level, Room 226 A

**1:45 PM EP12.02.01**  
**Low-Loss Metasurface Optics Down to the Deep Ultraviolet**  
Cheng Zhang, Shawn Divitt, Qingbin Fan, Wenqi Zhu, Anam Agrawal, Ting Xu and Henri J. Lezec; 1National...
Institute of Standards and Technology, Gaithersburg, Maryland, United States; College of Engineering and Applied Science, Nanjing University, Nanjing, China.

Recent years have witnessed the rapid development of flat optical elements, known as metasurfaces. With properly designed and arranged sub-wavelength structures over its plane, a metasurface can impart arbitrary, spatially variant amplitude, phase and polarization modulations on an incident electromagnetic wave. The highly customizable nature of a metasurface allows it to accomplish a variety of functions that have traditionally been fulfilled by a combination of different optical elements, such as gratings, lenses, polarizers, wave-plates, beam splitters, and hologram plates, with a significantly reduced physical thickness compared to traditional optical elements. So far, researchers have demonstrated various types of high-performance metasurfaces operating in the infrared (IR) and visible regimes, paving the way towards high-efficiency, multi-functional and compact photonic systems.

However, there has been a conspicuous lack of work in the ultraviolet (UV) region, which is the spectral range hosting an array of important applications such as photolithography, spectroscopy, sterilization, astronomy, medical therapy, and high-resolution imaging. High-performance metasurfaces working at IR and visible frequencies employ dielectric materials such as Si, TiO\(_2\), and GaN. Direct scaling of operation frequencies of metasurfaces based on these material systems down into the UV is challenging because of the intrinsically lossy response of such materials at wavelengths below their bandgap, preventing high output efficiencies.

Here, we show how low-loss metasurface devices operating at UV wavelengths down to the deep-ultraviolet range can be implemented using Hafnium Oxide, an amorphous dielectric material most commonly exploited as a high-static dielectric constant (high-\(k\)) material in integrated circuit fabrication, that is characterized by a wide-bandgap (5.8 eV). We demonstrate a variety of polarization-independent metasurface devices, including lenses, holograms and self-accelerating beam generators, operating at two near-UV wavelengths (364 and 325 nm) with efficiencies as high as 75\%. Scaling down metasurface critical dimensions, we realize holograms operating with high efficiencies of 60\% at a record-short, deep-UV wavelength of 266 nm. Finally, we demonstrate spin-multiplexed holograms and self-accelerating beams at 364 nm, and spin-multiplexed holograms at 266 nm.

2:00 PM *EP12.02.02
Enhanced Hot Carrier Effects in Ultra-Thin Metallic Films on Index Near-Zero Substrates
Jeremy N. Munday; University of Maryland, College Park, Maryland, United States.

Bulk metals are generally reflective and are therefore commonly overlooked as efficient absorbers; however, the fields of plasmonics and metasurfaces have given new insights into methods for turning reflective surfaces into absorbing ones. Another recent approach has been the use of subwavelength Fabry-Perot-like resonances in ultra-thin films, which has been used to achieve absorption above 70\%, approaching the theoretical limit using traditional substrates. Here we take a different approach and show that near-perfect absorption is achievable provided that the ultra-thin metals are deposited on an index near zero (INZ) substrate. In this talk, I will present the various design considerations that allow for ultra-thin metal films on INZ substrates to obtain near-perfect absorption throughout the visible spectrum and into the near-infrared (NIR). We find that metals commonly used for plasmonics and hot carrier devices, such as Au and Ag, can obtain near-perfect absorption for near-ultraviolet and visible wavelengths, while metals such as Pd and Pt are efficient absorbers throughout the near-ultraviolet to near-infrared spectrum. Finally, I will present results where we use this mechanism to enhance the photocurrent of photodetectors based on hot carrier generation in thin metal films.

2:30 PM EP12.02.03
High Contrast Grating Metasurfaces as Wavelength Selective Reflectors
Haley Bauser, Colton Bukowsky, Megan E. Phelan, David R. Needell and Harry Atwater; California Institute of Technology, Pasadena, California, United States.

High contrast grating (HCG) metasurfaces are promising alternatives to Bragg filters as wavelength selective mirrors. HCG metasurfaces consist of a single material layer with a high index of refraction (\(n=3\)) patterned at a subwavelength thickness directly onto a lower index (\(n=1.5\)) substrate. Bragg filters are highly efficient in reflection, but suffer from a strong dependence on angle of incidence. Moreover, Bragg stacks use many layers of different indices to manipulate light, resulting in an expensive fabrication process. In HCG metasurfaces, the high contrast between the respective materials’ refractive indices enables scattering and mode interference that results in a sharp and tunable reflection peak. We explore the design and fabrication of HCG metasurface mirrors using three different materials: aluminum antimonide, silicon, and silicon carbide. We optimize our design for application in a planar luminescent solar concentrator comprising mirrors cladding a planar waveguide with embedded quantum dot luminesphores emitting at a peak wavelength of 635 nm design to reflect quantum dot luminescence emission that couples with the band edge of a III-V photovoltaic cell. We fabricated HCG mirrors on glass substrates via sputtering or PECVD and patterning via e-beam lithography and a dry etch. We find that the ideal HCG for a peak centered at 635 consists of a hexagonal array of cylindrical pillars with the radius and height approximately 100 nm and a pitch of roughly 495 nm. The reflectance peak of these materials ranges from 80\% to 95\% at 635 nm.

2:45 PM BREAK

3:15 PM *EP12.02.04
Exotic Light-Matter Interactions in 2D TMDC Materials
Linyou Cao; Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Atomically thin two-dimensional (2D) transition metal dichalcogenide (TMDC) materials present a remarkable excitonic systems with exciton binding energy usually one order of magnitude higher than those in typical semiconductor materials. As a result, these materials bear great potential to enable the development novel optical and optoelectronic devices. Here we demonstrate some exotic light-matter interaction properties of 2D TMDC materials that result from the extraordinary strong exciton binding energy. This include: 1) giant gating tunability in the optical refractive index of 2D TMDC materials, in which a tunability > 60\% is achieved in the refractive index of 2D TMDC materials by electrical gating with a configuration compatible with CMOS devices; 2) room-temperature condensation, where the gas-like excitons may condense into a liquid-like state, electron-hole liquid (EHL). We will also demonstrate the magneto-optical properties enabled by magnetic TMDC materials.

3:45 PM *EP12.02.05
Robust and Scalable Meta-Surfaces for Powerful Lasers Applications
Eyal Feigenbaum, Jae H. Yoo, Hoang T. Nguyen, Michael A. Johnson, Salman H. Baxamusa, Selim Elhadj, Joseph T. Mckeown and Ibo Matthews; Lawrence Livermore National Laboratory, Livermore, California, United States.

The field of optical meta-surfaces is rapidly growing due to its great potential to enable thin optics implementation with relatively complex and flexible functions. In particular, high power laser systems could benefit from optical meta-surfaces that implement beam shaping, e.g., for wave-front aberration correction, but with the advantages of smaller accumulation of nonlinearity and lighter weight. Additionally, meta-surface technology could enable laser optics with improved anti-reflective layer designs. Current meta-surface technology is limited with respect to high power laser optics, which requires both scalability and laser intensity durability. The principal challenge arises from the necessity of patterning sub-wavelength features (to control the local optical properties by modifying geometrical properties) while being able to modify the structural parameters on the large optoelectronics scale used in high power laser systems (e.g., National Ignition Facility, Laser MegaJoule). The current patterning methods are either limited in scalability (e.g., FIB, e-beam lithography) or limited in robustness due to the usage of soft-materials (e.g., nanoimprint). We are developing novel technology capable of generating robust and scalable all-dielectric based meta-surfaces. In this talk we will describe the method, show results of fabricated meta-surfaces, and discuss the various levels of control that we have with this process. This method extends the current application field of interest for meta-surfaces to high power lasers, with the potential to stimulate meta-surface utilization in additional fields requiring large and robust optics.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-CONF-760584.

4:15 PM EP12.02.06
Highly Efficient Chiral Plasmonic Metasurfaces for Mid-Infrared Polarization Detection
Jing Bai, Chao Wang and Yu Yao; Arizona State University, Tempe, Arizona, United States.
Plasmonic metasurfaces provide great flexibility to control the amplitude, phase and polarization response of light in broad wavelength ranges from UV to THz, thus hold promise to realize ultra-compact chip-integrated photonic and optoelectronic devices for various applications. Chiral plasmonic metamaterial as artificial counterpart for the rare chiral material in nature enables generation, manipulation and detection of circularly polarized (CP) light. Plenty of works have demonstrated circular dichroism spectroscopy and circularly polarization detection based on chiral plasmonic metasurfaces. Besides, full Stokes parameters detector have been proposed based on phase gradient arrays, aperture antenna and in-line scatterers. Researchers are putting more efforts to develop new devices for high efficient and high performance polarization detection. Here we present our experimental demonstration of highly efficient (>85% transmission efficiency) chiral metasurface structures as circular polarization (CP) filters with extinction ratio over 50 (defined as the ratio between transmission of CP light with the desired handedness and that of the other handedness). The proposed structures are composed of rationally designed plasmonic antennas and nanowires, which are vertically intergraded with a subwavelength-thick dielectric spacer layer. This thickness of the device can be less than 1/10 of the operation wavelength. We investigated the design principle with anisotropic transfer matrix method and confirmed the design concepts with full wave simulation. According to our theoretical analysis, one can achieve CP filters with extinction ratio over 1000 and transmission efficiency over 90%. In experiment, we have achieved over 85% efficiency and extinction ratio ($r=T_{CP}/T_{CP}^*$) over 50 at 4 μm. We have also integrated the CP polarization filters with nanowire grating linear polarization filters on the same chip for full stokes polarization detection. The measurement errors of our devices are 2%, 4% and 5% for S1, S2 and S3, respectively. And the errors for DOLP and DOCP are 5.4% and 6.6%, respectively, which to our knowledge are the best among the metasurfaces based polarization detection techniques presented in literature so far. The operation wavelength of the device can be engineered from NIR to FIR (1 μm to 30 μm) by simply changing the design parameters. Our designs can be directly integrated onto various semiconductor-based photodetectors and imaging arrays; thus enable on-chip polarization detection and imaging for various applications such as circular dichroism (CD) spectroscopy, polarimetric imaging and sensing, and molecular spectroscopy.


4:30 PM EP12.02.07 Subwavelength Achromatic Metasurface Lens Over Whole Visible Bandwidths Ya Sha Yi, Yao Ye and Dachuan Wu; University of Michigan, Dearborn, Michigan, United States.

Metasurface lens is one of emerging planar nanophotonic devices that promises unprecedented control of the light at nano scale and have potential applications in highly multidisciplinary fields including imaging, sensing, spectroscopy and photovoltaics. Typically, for concentrating micro grating lens utilizing 0th diffraction mode, a high index contrast grating is used as individual phase shifter to satisfy the lens focusing requirements, as it can provide relatively large phase shift from 0 to 2π so that the light focusing condition can be met. However, the high index contrast gratings give rise to a significant chromatic behavior and achieving achromatic focusing over certain bandwidth turns out to be very challenging. The achromatic focusing capability is critical for a variety of applications, as light sources (e.g., light emitting diodes) or the signal (e.g., photoluminescence and fluorescence signals) has a substantial bandwidth, especially in the visible wavelength range. For refractive lens such as Fresnel lens, achromatic behavior requires hybrid design to compensate for chromatic loss, thus significantly increase the device’s complexity and cost. For emerging micro lens designed based on subwavelength phase shift units, metasurface based circularly polarized incidence is reported with achromatic behavior achieved through special dispersion control of Panchatramn-Berry phase elements. While for linearly polarized incidence, only several wavelengths can be achieved in telecommunication range, lens with a notable focal shift or very narrow bandwidth has been achieved.

In this work, we have demonstrated the achromatic all-dielectric metasurface lens covering the whole visible bandwidth based on relatively low index contrast gratings. Supported by the unique chromatic phase shift of polygonal polymer structure, we are able to design a broadband subwavelength achromatic micro lens which can cover 250 nm of visible bandwidths (from 435 nm to 685 nm) with focal shift less than 5% with linearly polarized incidence. Our work is a critical step further to achieve the promises made by the flat metasurface lens that is comparable with image qualities obtained by the commercial objective.

4:45 PM EP12.02.08 All-Dielectric Active Metasurfaces with III-V Multiple-Quantum-Well Mie Resonators Pin Chieh Wu,1,2, Ragip Pala,1 Ghazaleh Kafaie Shirmanesh,1 Wen-Hui Cheng,1 Ruzan Sokhoyan,1 Muhammad Alam1 and Harry Atwater1,2; 1California Institute of Technology, Pasadena, California, United States; 2Kavli Nanoscience Institute, California Institute of Technology, Pasadena, California, United States; Department of Photonics, National Cheng Kung University, Tainan, Taiwan.

Tunable metasurfaces enable active control of key constitute properties of light at a sub-wavelength scale. So far, electrically-tunable active metasurfaces in the near-infrared wavelength range have been typically achieved by incorporating active materials, such as tunable plasmonic structures or thermo-optically responsive media, into otherwise passive metasurface structures. To achieve a widely tunable response at low input power and high speeds in active metasurface structures, electro-optical modulation of resonantly excited quantum wells structures can enable strong light-matter interactions by couple of an optical field enhancement in an active material that can also undergo a large DC field modulation. Here, we report an all-dielectric active metasurface platform based on electro-optically tunable III-V multiple-quantum-well (MQW) Mie resonators. In this work, we design an epitaxial III-V compound heterostructure, comprising a distributed Bragg reflector (DBR) and a 1.23 μm-thick MQW layer grown on GaAs substrates. The DBR, which is used as a dielectric mirror, is comprised of 20 pairs of alternating layers of n-AlxGa1-xAs (76.5 nm) and n-GaAs (65 nm) with the n-AlxGa1-xAs as the topmost layer. We exploit the quantum-confined Stark effect in GaAs-based MQW Mie resonators to actively control the optical response of the metasurface phase and amplitude at near-infrared wavelengths. By applying a DC electric field across the Mie resonators, we dynamically modulate modes supported by the Mie-resonant metasurface elements. We experimentally observe a relative reflectance modulation of 270% accompanied with a continuous phase shift from 0° to 70°. In addition, we use our all-dielectric tunable metasurface to demonstrate a dynamically switchable diffraction grating. By selectively applying an electrical bias to metasurface elements, we can electronically modulate the metasurface period, enabling on-off switching of the first-order diffracted beam. We will also discuss how our tunable dielectric metasurface platform can be used for the realization of dynamically tunable ultrathin optical components, such as tunable metalenses, on-chip beam steering devices, active polarizers, and flat spatial light modulators.

References
Refractory nitride plasmonics offer the potential to realize enhanced light interactions for energy harvesting and photo-driven chemistry with materials systems that are thermally rugged, inexpensive, and potentially catalytic. Here, we have embedded commercial and in-house synthesized titanium nitride (TiN) nanoparticles into matrixes of titanium dioxide (TiO$_2$) and compared their ability to enhance electrochemical oxidation reactions to that of conventional gold (Au) nanoparticles. Although the photon-to-carrier conversion efficiencies were low (~10$^{-3}$%), the reaction rates were enhanced by a factor of 4 in the visible and near-infrared for Au and TiN, respectively, compared to a pure TiO$_2$ control. The spectral dependence of reaction rate enhancement followed the nanoparticle extinction spectra and a linear power-dependence identifies a photo-excited carrier mechanism (i.e., decaying plasmons excite carriers which participate in chemistry rather than heating of the system). Lastly, photo-induced transients of the electrochemical signal are found to be consistent with the band structures of these heterosystems. Specifically, the TiN/TiO$_2$ system, which has little or no Schottky barrier, exhibits a bias-dependent photoelectrochemical response rate while the Au/TiO$_2$ system, which naturally forms a Schottky barrier that immediately separates charged carriers, exhibits a near-instantaneous response.

Plasmon Effect Study in Lithium Borate Glasses Doped with Dy$^{3+}$ and Yb$^{3+}$ and Containing Silver Nanoparticles 

In this work, it was synthesized and characterized Lithium Borate Glasses doped with rare earths and containing Silver nanoparticles in different concentrations. The rare earths employed were Dy$^{3+}$ and Yb$^{3+}$. The Scanning Electron Microscope (SEM) show the formation of Silver nanoparticles, absorption spectra of the samples show the presence of bands in 420nm and 450nm associated with the SNP (Plasmon effect), and 750nm, 800nm, 875nm, 1098nm and 1278nm belonging to the Dy$^{3+}$ and one large peak in 976nm belonging to the Yb$^{3+}$. Emission spectra show two prominent bands in 480nm, 574nm, and one faint band in 665nm, all bands under 364nm pumping, and the fluorescence in the 550nm and 590nm spectral range enhanced two bands. It was studied the Plasmon Effect due to the increment of the SNP in the samples.

Colloidal Gold Nanoplate-Based Heterodimers for Charge Transfer Plasmon and Fano Resonances

The fascinating optical properties of noble metal nanocrystals are intriguingly offered by their localized surface plasmon resonances. Hybridized plasmon modes can be produced by placing two plasmonic nanocrystals close to each other. The electromagnetic interaction between the hybridized modes possesses unique plasmonic features, such as electromagnetically induced transparency, Fano resonance, magnetic plasmon resonance, and charge transfer plasmon (CTP). Plasmonic Fano resonance arises from the destructive interference between a broad, superradiant and a narrow, subradiant plasmon mode that overlap spatially with each other. It features an asymmetric non-Lorentzian spectral profile with a narrow transparent window corresponding to the energy of the subradiant plasmon mode. The unique properties of Fano resonance help in revealing the underlying physics in many intriguing phenomena and make it promising for many plasmonic-based applications, such as sensing, plasmonic switching, light slowing and stopping. However, most metal nanostructures cannot only support several Fano resonances with relatively shallow dips in the visible and near-infrared ranges. Second, when the air or vacuum gap between two metal nanoparticles is smaller than ~0.3 nm, the classical electromagnetic framework breaks down and the quantum tunneling effect alters the plasmon coupling behavior substantially. A new CTP mode emerges as a characteristic signature of the interparticle electron tunneling across the junction. However, it has still been challenging to fabricate plasmonic nanocavities with ultrasmall gaps. In this regard, bridging molecular junctions have been introduced to allow electrons to tunnel across the gap with a moderate distance. Nonetheless, the observed CTP has been limited with dipolar plasmon modes.

Colloidal Gold Nanoplate-Based Heterodimers for Charge Transfer Plasmon and Fano Resonances

We have fabricated gold nanoplate (NPL)-nanosphere (NS) heterodimers and observed Fano resonance with a deep dip (Nanoscale 2017, 9, 13222). When a gold NS is attached to one sharp vertex or one edge of a gold NPL on an indium tin oxide (ITO) substrate, a strong polarization-dependent Fano resonance with a deep dip is observed in the scattering spectrum. Under in-plane excitation that is polarized perpendicular to the connection axis between the NPL and NS, the Fano resonance can be “switched off”. In addition, by positioning a gold NS at the top facet of a gold NPL on a silicon substrate, the dipole–octupole interaction between the NS and NPL also gives rise to a deep Fano dip under out-of-plane excitation (Nanoscale 2016, 8, 17645). The dip depth and asymmetric line shape of the Fano resonance possessed in both structures can be well tailored by varying the sizes of the involved nanocrystals. When the gold NS and NPL are separated with a self-assembled monolayer of conductive molecules, electrons are allowed to transfer across the molecular junction. The electron tunneling effect largely modifies the Fano resonance feature in the scattering spectra, as well as the observation of a higher-order CTP. Taken together, these results will be helpful for deepening the understanding of Fano resonance and electron tunneling in plasmon-coupled systems, picturing a promising future in developing various potential applications, including nonlinear and switched metamaterials, displays, nanonanotransistors, optoelectronics, and new types of molecular-plasmonic devices.
resistive in the other directions. To explore the link between the non-local dielectric constant and the heterogeneous electron transfer rate, cyclic voltammetry has been used to observe the rate constant of the heterogeneous electron transfer from Fe$^{3+}$ to Fe$^{2+}$ on a Au surface.

In this report, the dependence of sweep rate on the electron transfer rate and potential on Au surfaces was measured to determine the carrier diffusivity and rate constant for the electron transfer reaction between an outer sphere redox reagent, ferricyanide, Fe(CN)$_6^{3-}$, and gold. Though the surface immediately adjacent to the ferricyanide ion are the same Au film, an enhancement in the electron transfer rate constant has been observed in the vicinity of the metamaterials. This rate constant was observed to six times faster than a single thin gold layer (~25 nm) from which the metamaterial is constructed. This enhanced electron transfer rate constant was also three times faster than thick gold (~200 nm) which is the thickness of the metamaterial stack. Future work will examine the effects of the dielectric constant on the rates of the forward and reverse rate constants.

**EP1.03.06**
Ultra-Sensitive microRNA Detection Using Vertically Coupled Plasmonic Nanoantennas Xiahui Chen$^1$, Zhi Zhao$^1$, Jiawei Zuo$^2$, Yu Yao$^2$ and Chao Wang$^2,1$.
$^1$School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States; $^2$Center for Photonics Innovation, Arizona State University, Tempe, Arizona, United States.

Early and accurate diagnosis of cancer is extremely important for cancer treatment and improving patients’ survival rate. Liquid biopsy is an emerging approach that detects a panel of biomarkers that are available in bodily fluids, and potentially allows noninvasive diagnostics of a broad variety of cancers. Among the most studied biomarkers, microRNAs (miRNAs, single-stranded oligoribonucleotides) are viewed promising candidates, as they function as both oncogenes and tumor suppressors. The dysregulation of miRNAs has been shown to strongly correlate to the proliferation of cancer cells in various types of cancers. Current major approaches for miRNA detection rely heavily on enzymatic reactions that usually introduce biases, demand special instrument, and require long processing time. On the other hand, plasmonic nanoantennas have attracted considerable attentions due to its ultrahigh sensitivity, design flexibility, label-free detection and low instrument cost. However, miRNAs only have relatively small modulation of refractive index near the sensor surface due to their short sequence (~20 bp, or ~7 nm in length), and hence usually results in small optical signals that is insufficient to accurate diagnosis.

Here we present a vertically coupled complementary structure, consisting of a nanobar antenna and a perforated nanoslit aperture antenna separated by SiO$_2$ nanopillar. This structure has shown a high sensitivity of 1.36 nm shift in detecting assembled 1-octadecanethiol in the mid-IR range (ACS Nano, 2017, 11 (8), pp 8034–8046). In our ongoing work, we design nanoantennas at visible and near-IR wavelength range, and optimize its sensitivity through vertical coupling between the nanobar and aperture antennas and horizontal coupling between adjacent nanobar antennas. Our full-wave simulation shows that the captured miRNA on the sensor surface can lead to ~23-30 nm shift upon miRNA hybridization to DNA probes. In our preliminary experiment, we assembled thiolated single-stranded DNA probes to the sensor surface, and demonstrated 13 nm resonance shift upon miR-10b hybridization at 100 pM concentration, which is comparable to the state-of-the-art research (~8.5 nm at same concentration). Currently we are evaluating the detection limit of the miR-10b on our plasmonic nanoantennas and studying the specificity using different probe designs. We expect to update our results at the conference. Our concept of plasmonic nanosensing can be widely extended to more complex structures and used for multiplexed detection, which have broad applications in early, low-cost, and portable cancer diagnosis.

**EP1.03.07**
Hybrid Metal-Dielectric-Metal Structures of Controlled Geometry, Based on Large Area Colloidal Lithography with Metallic Spheres as a Patterning Mask Jusung Park, Sungjin In and Namkoo Park; Seoul National University, Seoul, Korea (the Republic of).

With the recent development of precision lithography such as EBL, FIB, and EUV technique, it now became possible to overcome the stringent requirements of nano-scale offset, high step-coverage and sub-wavelength resolution [1], in the fabrication of nano-photonic structures. These efforts, especially toward visible regimes, have also enabled promising applications such as display [2], antenna [3], color filter [4-5] and information encoding [6-7] over recent years. Nonetheless, in view of the costs, non-scalable, equipment dependent and time-consuming processes involved in the precision lithography techniques, the realization of cost effective, litho-free, and large-area fabrication of nano-photonic structures still remains as a challenge.

In this work, we present a colloidal lithography which uses metallic spheres as a patterning mask, to achieve hybrid metal-dielectric-metal (MDM) structures of controlled geometry in a large-scale. By adjusting the etching conditions between the metal- or dielectric preferential settings, the eccentricity of metal spherical and height of dielectric pillar are adjusted for the fine tuning of coupling strength between the residing hybridized modes, and therefore to deliver significant modulation of the reflection spectra in the visible regime (400nm – 800nm). Control of the full width at half-maximum (FWHM) bandwidth from 50nm to 250 nm, and near-perfect absorption (> 95%) at the resonance wavelength are demonstrated, for future applications in colored light harvestings, anti-counterfeittings and anti-reflecting coatings. As a simplest demonstration, we will present a large-area (> 4 inch) and full gamut color filter, with iridescent response. Our result of large-area, litho-free colloidal metal-particle mask technique will offer a new path in the fabrication of cost-effective and fabrication-friendly, precision nano-photonic devices.

**REFERENCE**


**EP1.03.08**
Silicon Surface Nanotexturization with Diffraction Gratings via Metal-Assisted Chemical Imprinting Aliaksandr Sharshenous, Stanislau Niazuorazh, Michael Gregory, Vijay Pentapati, Jasmina Markovski and Bruno Azzeredo; Arizona State University, Mesa, Arizona, United States.

Metal-assisted chemical imprinting (MAC-imprinting) is a combination of metal-assisted chemical etching (MACE) and nanoimprint lithography (NIL) that can selectively etch arbitrary and complex 3D microscale features in silicon wafers such as parabolas, parabolic cylinders [1], inverted pyramids [2], rectangular grooves and holes [3]. The patterning resolution of this process can be controlled by varying etching parameters such as solution composition or external bias [4] down to the sub-5 nm range. Thus, this process can deliver mirror-finish surfaces suitable for manufacturing of optical elements such as lenses and gratings in which low surface roughness is critical. In this paper, we demonstrate MAC-imprinting of diffraction gratings onto Si wafers and examine the pattern fidelity and roughnesses across stamp and substrate. MAC-imprinting stamps consisting of patterned SU-8 with periodic linear grooves were prepared using UV-NIL. Patterned SU-8 was then coated with a Cr adhesive layer and an Au catalytic layer by magnetron sputtering, and used in MAC-imprinting of p-type low-doped (100) Si wafer. Visual examination of imprinted Si chips revealed surfaces exhibiting diffraction pattern similar to its corresponding stamps. Analysis of SEM data determined a width of 0.54 μm and period of 902 nm of the imprinted groove corresponding to the same values of stamp features. According to AFM-analysis surface roughness of the grooves was approximately 18 nm (RMS) matching the surface roughness of the MAC-imprinting stamp features. Thus, the origin of the roughness was attributed to the grain size of the sputtered Au layer rather than to the MAC-Imprint process itself. As a result, MAC-imprinting of diffraction gratings onto Si surface was successfully performed and the imprinted groove’s width, period and surface roughness was found to match the corresponding values of the imprinting stamp. This result serves to validate the use of MAC-imprinting to fabricate optical elements with superior quality.

**Bibliography**


**EP1.03.10**
Plasmon-Enhanced Emission and Quenching of Metallic Emitters Soheila Mashhadi1, Maxim Durach2, David Keene1 and Natalia Noginova1; 1Norfolk State University, 2Center for Nanoscale Materials, Argonne National Laboratory, 3Department of Physics and Astronomy, North Carolina State University.
Possibility to control spontaneous emission via modified optical environment provides new opportunities for magnetic dipole transitions, which are commonly very weak in comparison with electric transitions. We discuss various approaches for enhancing magnetic transitions. In particular, we concentrate on effect of propagating surface plasmon polaritons on emitters located in very close vicinity of plasmonic metal. In comparison with electric dipoles, magnetic emitters have lower quenching, and practically the same efficiency of SPP excitation. This prediction is confirmed by experiment using spontaneous emission of Eu³⁺ ions at magnetic dipole and electric dipole transitions.

EP12.03.13
Design of Ultrawide Bandwidth Electromagnetic Wave Absorbers Using Frequency Selective Surfaces with Different Patterns and Geometries

With the increased use of electronics over the broad frequency spectrum from microwaves to millimeter waves, high-performance absorbing and shielding materials are needed to ensure electromagnetic wave control and compatibility. Acquisition of wide bandwidth absorption with a planar layer and a small layer thickness has been a major challenge for commercial and military applications. Unfortunately, it is a difficult task to achieve both bandwidth enhancement and thickness reduction simultaneously because of an inverse proportional relationship among the bandwidth, thickness, and reflectance of the absorbers. In this study, the design of a thin and ultra wide-bandwidth microwave absorber has been conducted by layering two frequency selective surfaces (FSS) with different patterns (square loop, patch) and geometries on the grounded dielectric substrate. The circuit parameters of inductance and capacitance of the FSS are retrieved using the equivalent circuit model and utilized in the design of the wide-bandwidth absorber. Optimal design for the surface resistance of the FSS and spacer thickness of the double-layer absorber provides very large absorption bandwidth and small total thickness (for FSS of square-loop geometry, for instance, 10 dB bandwidth is 5.2 – 38.3 GHz and total thickness of the absorber is 6.3 mm, which is very close to the theoretical limit). Admittance analysis for substrate (layer thickness) and FSS (patterns, geometries) is made for the design scheme of the ultrawide bandwidth absorber. The free space measurement result with a test sample prepared by the screen printing method was in good agreement with the simulation result and strongly verified the validity of proposed design method. For these periodic array structures, however, the grating lobe or high frequency harmonics were observed in the high frequency region above which the unit cell periodicity is larger than the wavelength, and as the incidence angle increased, the grating lobe occurred at a lower frequency for both TE and TM polarization. The unit cell periodicity must be controlled in the periodic array structure, particularly for large oblique incidence angles.

SESSION EP12.04: Composites and Metastructures

8:30 AM *EP12.04.01
Quantum Emission and Nonreciprocal Optical Transmission in Deeply Subwavelength Systems

A revolution in materials discovery has yielded a diverse portfolio of new classical and quantum photonic materials. In particular, a variety of two-dimensional layered architectures can be crafted with structural precision approaching the atomic scale. In parallel, advances in nanophotonics, plasmonics, and metamaterials have enabled precise control of light-matter interactions down to the nanoscale. By combining concepts from both of these young and rapidly developing fields, there is now an opportunity to create phononic matter where optical properties are tailored to attain thermodynamic limits. Here, we present our research exploring ultrathin nanostructured materials and metamaterials for bright quantum emission and nonreciprocal optical transmission. First, we correlate the local atomic structure of color centers in van der Waals materials with their optical emission at a single defect level. We use transmission electron microscopy and cathodoluminescence spectroscopy to investigate color centers in two-dimensional hexagonal boron nitride. This wide bandgap material is capable of room-temperature, high-brightness visible quantum emission, though the atomic structure of color centers remains unknown. Through high-resolution spatial maps, we find that multiple quantum emitters reside within a ~100nm region, each contributing slightly distinct spectral signatures. Defects are found in locations usually associated with regions of high strain and dislocations. Through correlation of cathodoluminescence to photoluminescence, we show that two classes of emitters exist, including charge neutral and charged emitters. Importantly, all are stable upon multiple exposures to the electron beam.

Next, we introduce nanophotonic designs that enable nonreciprocal transmission of visible and near infrared light within subwavelength optical paths. We show that the Kerr effect, in which the refractive index depends on the local light intensity, can produce passive directional transmission. In this case, slight structural asymmetries lead to a directionally dependent field enhancement and, consequently, a directional Kerr shift of the resonant dip. We achieve nonreciprocal transmission for silicon films as thin as 100nm with incident powers of a few kW/cm². We additionally show a nonreciprocal Kerr shift in a phase gradient metamaterial, making nonreciprocal beamsteering and lensing possible. This platform enables time-reversal-symmetry breaking for arbitrary free-space and modal optical inputs in a simple, robust materials platform, with potential for creating nanoscale optical diodes and photovoltaic devices that violate Kirchhoff’s law.

9:00 AM EP12.04.02
Towards Compact Infrared Adaptive Optics by Local Tuning of Nanophotonic Structures Enabled By Phase-Change Materials

Despite their nanometer thickness, metamaterials comprised of resonant metallic or dielectric nanostructures offer comprehensive control over light fields and allow for the creation, detection and transformation of light. Often, their optical functionality is only obtained at a fixed wavelength, determined by the geometric design and the material properties. For optimal functionality, they need to be freely programmable and have low optical losses. Phase-change materials (PCMs) provide a switchable dielectric environment for resonant nanostructures, altering their resonance frequencies in a non-volatile, reversible way. PCMs have a high optical contrast between their amorphous and crystalline phases, while only exhibiting low optical losses in the infrared [1,2]. Using PCMs for active metasurfaces offers adjustable, designed functionality for manipulation of light. Among recent examples are polarization filters [3], beam steers and lenses [4]. During crystallization of the PCM on a hot plate, intermediate states of the PCM have also been exploited to obtain gradual resonance shifts [5,6]. These shifts due to partial crystallization are uniform over the whole metamaterial and usually described by effective medium theory.

We now show how we can simultaneously control the size, position and crystallization depth of the switched phase-change volume within each meta-atom to selectively tune its optical properties. By using visible light for switching an infrared metamaterial, we could modify the PCM phase on length scales which are smaller than the size of a meta-atom. When combining this with present designs for infrared metamaterials, it will become possible to program the reflection amplitude and phase of each individual meta-atom. This goes beyond effective medium concepts, especially when accounting for the spatially localized electric near-fields of nanoantennas in the meta-atoms. With the proposed concept, it should be possible to actively impart multiple complex functionalities onto the same metasurfaces or to make small adaptations to correct external aberrations and fabrication errors.

References
Copper and Aluminum Island Films as Plasmonic Structures for Solar Energy Conversion

Chalcogenide Phase-Change materials (PCMs) exhibit high magnetic-optic contrast between their amorphous to crystalline states. The switching between such states can be quickly and reversibly controlled on demand, by making use of different heat stimuli such as electrical, thermal or optical pulses [1]. For the last couple of decades, PCM applications have been therefore focused on the development of non-volatile electrical and optical memories [2]. More recently, however, PCMs have attracted much interest as a tunable element in plasmonic optical metasurfaces [3, 4], due to the fact that PCMs have very different refractive indices when in amorphous and crystalline states, but can also provide intermediate crystallization levels having optical properties lying between those of the two structural phases. In this work, therefore, the potential of phase-change “meta-devices” is illustrated via the introduction of various device prototype concepts in which the state (fully-crystalline, partially crystalline or fully amorphous) of the PCM layer can be used to control device functionality.

As a first example, by appropriately combining plasmonic metasurfaces with the well-known phase-change alloy Ge2Sb2Te5, we have developed a dynamic beam steering meta-device working in the near infrared (specifically at λ = 1550 nm). As a second proof-of-concept, we demonstrate that thin films made of GeTe (another widely employed PCM), can be used to create broadband amplitude-only modulators in the visible regime. In such devices, the amount of light reflected can be controlled via changing the fraction of crystallization of the GeTe active layer, without introducing any optical phase shifts during the process (i.e. we can create an amplitude-only modulator). Finally, we show that optical phase manipulation is also possible over a 2π range, by combining novel low-loss PCMs (here Sb2S3) [5] with all-dielectric asymmetric Fabry-Perot cavity inspired metasurfaces [6]. Our approach here consists of arrays of geometrically identical elements (or meta-atoms) where the optical phase can be locally tuned between 0 and 2π at a wavelength of λ = 850 nm (commonly used in biomedical diagnostics) by changing the level of crystallization Sb2S3 in a pixelated device.

We believe that PCM-based metasurfaces and meta-films, such as the ones presented here, could be well-suited for many exciting applications, such as optical telecommunications, LIDAR scanning systems, autonomous vehicles, reflective displays, holography or wavefront shaping in biological tissues.

References:
[6] C. Ruiz de Galarreta et al., ISCAS 2018 (Florence, Italy)
that Cu and Al metal island films can represent an efficient low-cost platform for certain plasmonic applications such as solar energy harvesting.


This talk will review our recent work on exploring functional plasmonics (i.e., switching, plasmonic Coulomb blockade) achieved in subnanometer gaps at the transition point towards tunneling. This is an ultra-sensitive plasmonic platform, akin to the metal-insulator transition achieved bulk materials like vanadium dioxide; however, subnanometer gaps provide a designer-based approach to switching.

I will also discuss our recent work on dual-wavelength upconversion and upconversion from single upconverting nanocrystals trapped optically within an aperture in a metal film. We demonstrate that tuning the aperture dimensions can have a massive impact on the upconversion detected.

**11:15 AM EP12.04.08 Inkjet-Printing of Plasmonic Reflective Displays** Samim Sardar, Pawel Wojciech and Magnus Jonsson; Laboratory of Organic Electronics, Linköping University, Norrköping, Sweden.

Plasmonic color generation have attracted tremendous interest in recent years as a solution for ink-free color printing. The prominent advantages of plasmonic coloration are better robustness compared with organic dyes while also providing high chromaticity and brightness. However, use of costly nanofabrication techniques to make reflective displays restricts potential applications and production of functional devices. Here, our aim is to generate plasmonic structural colors at high resolution using inkjet printing, which is scalable to large areas and avoids complicated fabrication steps. Our plasmonic metasurfaces contain three solid films on flexible plastic substrates. A silver film (~500 nm) was first inkjet-printed on the substrate to provide a high base reflection. Then an organic material was printed as a dielectric spacer layer with varying thicknesses to tune the reflective color by Fabry–Perot interference. A semi-transparent plasmonic top mirror completes the cavity and also improves color generation via wavelength-dependent plasmon absorption. Here, I will present our work towards facile fabrication of structural colors and discuss our results based on reflectivity measurements of red, green and blue pixels using micro-spectroscopy. We believe this inkjet printing process has the potential to generate reflective displays with high resolution, low cost, flexibility and compatible with large-scale production.

**11:30 AM EP12.04.10 Nonnegative Quadratic Programming Optimization of Focused Ion Beam Fabricated 3D Nanostuctures for Structural Colors** Vivek Garg1, 2, 3, Rakesh Mote2 and Jing Fu1;1 IITB Monash Research Academy, Mumbai, India; 2Indian Institute of Technology Bombay, Mumbai, India; 3Monash University, Melbourne, Victoria, Australia.

Structural colors, originated from interaction of visible light with subwavelength nanostructures, offer high spatial resolution color printing, beating fundamental resolution limit of a light field optical microscope. Such structural colors, arising from resonant scattering of light from subwavelength nanostructures, can be printed at resolutions as high as ~100,000 dots per inch (DPI). A variety of design, methods have evolved over the years for structural color generation and color printing at optical diffraction limit of light1. A novel approach, utilizing focused ion beam (FIB) direct fabrication of high-index silicon (Si) 3D photonic nanostructures for multicolor generation with enhanced color purity and high resolution color printing applications was recently developed2. Although successful, the systematic variation of geometrical parameters for tuning of color performance can be quite cumbersome sometime and require significant time and experiments, and does not necessarily allow tailoring the chromatic response in an optimal way prior fabrication. In this work, a general framework for optimization of photonic nanostructures for multicolor generation is presented. The design of photonic nanostructures for desired color printing is optimized numerically through the formulation of a nonnegative quadratic programming problem. This problem is solved by an iterative approach based on multiplicative updates algorithm3 for an optimal solution of ion beam dwell time maintaining high accuracy. The optimization algorithm is aimed at minimizing the deviation of a simulated geometry by FIB fabrication from the desired geometry of photonic nanostructures for color printing. The optimization algorithm for Si photonic nanostructures to develop structural color printing is further coupled with electromagnetic simulations based on finite-difference time-domain (FDTD) calculations. The chromatic response of periodic subwavelength nanostructures is calculated using FDTD simulations. The numerical results show that this hybrid approach is a versatile tool for the design of photonic structures for multicolour generation, which can be extended for different design and application perspectives. In summary, this work provides a general framework for design and optimization of photonic nanostructures for multicolor generation. This will enable automatic design of photonic nanostructures for high resolution structural color printing applications with ion beams. The possible ways to expand the color gamut and improve the color performance of such photonic color filters on CIE 1931 (Commission Internationale de l’Eclairage) color space will be further discussed. Finally, such optimization of photonic nanostructures is not just limited to structural color printing and has tremendous potential for future optics offering unique opportunities for optical security, polarimetry, spectral imaging applications etc.

(2) Garg, V.; Mote, R. G.; Fu, J. Focused Ion Beam Direct Fabrication of Subwavelength Nanostructures on Silicon for Multicolor Generation. Advanced Materials Technologies 2018, 3 (8), 1800100.


An idea “to marry” silicon as a semiconductor material with noble metals to fabricate a highly ordered plasmonic nanostructures has been an obsessive dream of specialists in metamaterials for photonics, surface enhanced vibrational spectroscopy, optoelectronics, etc. Porous silicon is one of the most favorable materials to achieve this objective as it can be used as a tool for integration with silicon technology. Metamaterials must have an ordered periodical structure. However porous silicon, which is traditionally formed by an electrochemical etching of monocryrstalline silicon, is typically characterized by a significant deviation of geometrical parameters of pores up to 50%. This leads to non-reproducibility of morphology of plasmonic nanostructures depositing on such porous material. In present paper, we developed a novel metal-assisted electrochemical method to obtain extremely ordered structure of mesoporous silicon with pore diameter deviation less than 10%. Following deposition of thin films of coinage metals was shown to provide a formation of so-called plasmonic nets composed of periodically crossing nanowires. Simulation of an electric field in the cavities of these nets showed its localization in the pore mouths due to strong rim component. It is proposed to use the profit of this component in the surface enhanced Raman-scattering (SERS) spectroscopy to detect and study analytes at submolar concentration down to the single molecule level. To place analyte species in the pore mouth we used sandwich film of graphene-test molecule-graphene covering the plasmonic net. Graphene was found to play a role of support for analyte molecules and a protection for heat sink induced by laser excitation. In addition to the improved plasmonic properties of the coinage metals organized into net on modified mesoporous silicon, the paper also presents a description of changes in magnetic and catalytic properties of other metals deposited on the developed template.

SESSIO EP12.05: Nanostuctures
Session Chairs: Kuo-Ping Chen and Ann Roberts
Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 226 A

**2:00 PM EP12.05.02 Localized Surface Plasmon Modes in Nanoparticle Arrays and Dimers** Viktoria Babicheva, John Nehls, Jerome Molenoy, Aoxue Han and Colm Dinneen; College of Optical Sciences, The University of Arizona, Tucson, Arizona, United States.
Plasmonic nanostructures can significantly enhance electric and magnetic fields at nanoscale dimensions. Fields localized in the narrow gaps of plasmonic nanostructures can be several orders of magnitude higher than the incident light field, and this field enhancement strongly affects light-matter interaction processes in plasmonic nanostructures. Here, we study field enhancement in nanoparticle dimers and analyze surface plasmon amplification by stimulated emission (spaser) in the dimer gap. We consider both sphere and disk silver nanoparticles and employ finite-difference time-domain simulations for modeling field enhancement in the dimer.

Our in-house finite-difference time-domain (FDTD) method includes non-uniform, geometry-specific, semi-conformal meshing of the nanostructures and enables accurate resolution of electromagnetic ‘hot spots’ in the nanoparticle gap without parasitic staircasing. Our technique allows for FDTD simulation of fully-anisotropic permittivity and permeability material tensors. Semi-conformal meshing is enabled by placing grid boundaries along the surfaces of devices in critical areas and Maxwell’s equations encapsulating a coordinate transformation into the material tensors.

Using this approach, we numerically observe gap modes with even and odd field distributions within the 10-nm dimer gap and identify spatial regions with nodes and anti-nodes of the field enhancement. We use quantum density matrix (optical Bloch) equations for the spacer, calculate the plasmon amplification in the gap, and show its correspondence to the total mode characteristics. Because of the strong field enhancement in the gap, amplification of plasmons in a nanoparticle dimer is more efficient than ones in the proximity to a single nanoparticle and can be used as an ultra-compact light source in optical devices and medical applications.

Acknowledgment. This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. FA9550-19-1-0032.

References:

2:15 PM EP12.05.03
3D Nanocrystal/Bulk Heterostructures with Giant Chiroptical Properties
Jaeck Guo1, Mingliang Zhang1, Ji-Young Kim1, Aaron Stein2, Nicholas Kotov3, Christopher Murray1 and Cherie R. Kagan4, 1Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Materials Science and Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 4Brookhaven National Laboratory, Upton, New York, United States.

We report a novel fabrication method that exploits the differential chemical and mechanical properties of colloidal nanocrystals (NCs) and bulk materials to transform 2D bilayer heterostructures into 3D architectures by design. Colloidal NCs are hybrid systems, composed of inorganic cores and organic ligand shells, which make their surfaces chemically addressable and their assemblies mechanically soft. Using ligand exchange methods, bulky ligands that originally stabilize as-synthesized NCs are replaced by more compact ligands within a few minutes. Ligand exchange triggers a large volume shrinkage in NC assemblies, and in bilayer NC/bulk heterostructures generates a large misfit strain that drives bending. Following this strategy, we establish a set of design rules to create various 3D, cell-sized superstructures. These 3D structures may be harvested from surfaces and suspended in solvents or they can remain bound to surfaces. By choosing different colloidal NC building blocks, we demonstrate the versatility of this technique to create 3D structures with unique optical and magnetic physical properties. For example, we apply the design rules to construct 3D metasurfaces with giant chiroptical properties.

2:30 PM BREAK

3:30 PM EP12.05.04
Spectroscopic Nanotransducers for Infrared Sensing Applications
Tadaaki Nagao1, 2; 1National Institute for Materials Science, Tsukuba-city, Japan; 2Department of Condensed Matter Physics, Hokkaido University, Sapporo, Japan.

Wavelength-selective light absorbers and emitters, or spectroscopic energy transducers for light, are expected to provide wide variety of applications in energy harvesting, remote sensing, and label free bio-sensing. By utilizing the strong near field of optical antennas and metamaterials, strong signal enhancement of molecules becomes operative to realize high sensitivity vibrational sensing. Recent developments in infrared plasmonic materials, nanostructure fabrication techniques, as well as their surface functionalization techniques have enabled us to propose and fabricate various types of advanced nano-sensing devices. In this talk, we exemplify the detection of tiny amount of molecules by surface-enhanced infrared absorption spectroscopy, using Au infrared antennas and metamaterials. We also introduce our new approach utilizing infrared surface plasmons in optical antenna array made of phosphonic acid-functionalized ITO nanorods to detect proteins with high specificity and sensitivity. In the latter half of the talk, we introduce some of our recently developed uncooled infrared sensors combined with spectroscopic perfect absorbers for wavelength-selective infrared ray detection. The MIM metamaterial IR sensors with pyroelectric detection as well as thermoelctric detection exhibit resolutions better than 1um with wide acceptance angles. By adopting Gires-Turnmois structure with plasmonic metals, the wavelength resolution goes lower than 50 nm at resonance wavelength of 3-4 um. Such structures also shows sharp thermal emission when it is fabricated with low-loss materials and heated at high temperatures. These devices will open a new avenue for potential applications in multiband temperature sensing, infrared-color imaging for material sensing, and NDIR gas sensors for security gas sensors and combustion analysis.

References:

4:00 PM EP12.05.05
Spectroscopy, Characterisation and Applications of Plasmonic Sodium Tungsten Bronze Nanoparticles
Levi Tegg1, Dylan Cuskelly2 and Vicki J. Keast1; 1School of Mathematical and Physical Sciences, University of Newcastle, Callaghan, New South Wales, Australia; 2School of Engineering, University of Newcastle, Callaghan, New South Wales, Australia.

The noble metals, particularly Au and Ag, are widely used as plasmonic materials. Although Au offers terrific chemical stability and several options for nanofabrication, it suffers from relatively high plasmon damping losses. In contrast, Ag has very strong plasmon resonances but corrodres under ambient conditions, limiting device lifetimes. The limitations of Au and Ag has fuelled the search for alternative plasmonic materials.

The sodium tungsten bronzes (Na2WO4) are sub-stoichiometric metal oxides with variable Na content, 0 ≤ x ≤ 1. Above x > 0.3, the intercalated Na donates its 3s electron to the WOx conduction band, giving Na2WOx metallic electrical and optical properties which vary with the Na content. From electron energy-loss spectroscopy (EELS) studies, Na2WOx has been shown to support strong bulk plasmon resonances which blueshift with increasing x, from near-infrared to visible frequencies. However, characterisation of localised surface plasmon resonances (LSPRs) has been limited due to the lack of fabrication techniques for Na-rich (x > 0.5) nanoparticles.

Here, we demonstrate the synthesis of Na2WOx nanoparticles across 0.41 ≤ x ≤ 0.83 using a high-temperature method. Results from ex-situ and in-situ diffraction techniques provide insight into optimising the synthesis procedure to minimise the particle size of the products and to maximise phase-purity. Spectrophotometry and spatially-resolved EELS are used to investigate the plasmonic properties of Na2WOx. Strong LSPRs are observed which increase in frequency with x, similar to the variation in the bulk plasmon frequency. Experimental results are supported by simulated responses, which are calculated using the boundary element method (BEM).

Based on experimental and calculated responses, potential applications in solar control filtering, plasmon-assisted photovoltaics and plasmonic photocatalysis will be discussed. Given their high chemical stability, simple nanoparticle fabrication and tunable optical properties, we show that the sodium tungsten bronzes are promising alternative materials for plasmonics.

4:15 PM EP12.05.06
Non-Resonant Enhancement of Second-Harmonic Generation in a Dielectric Micro/Nano-Hybrid Particle with a Nonlinear Metamaterial Shell
Joong Hwan Bahng1, Douglas G. Monjoy2, Saman Jahani3, Nicholas Kotov4 and Alireza Marandi5; 1California Institute of Technology, Pasadena, California, United States; 2Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States;
Nanoscale particles are a promising class of materials for optical nonlinear conversion because of the strong field localization and the phase-matching-free conditions. While their utilities are envisioned in a spectrum of applications, a general layout to achieve and enhance nonlinear conversions is barren. The Mie and plasmonic resonances have been utilized in nano-scale particles to enhance the nonlinear response, especially the second-harmonic generation (SHG). While showing great promises, geometrical and bandwidth constraints in resonant enhancement, as well as loss and synthetic complexities in embedding plasmonic constituents impose challenges. In this study, we experimentally demonstrate an approach to achieve and enhance optical nonlinear conversion through a non-resonant dielectric particulate platform. The platform is based on a dielectric microsphere with a nonlinear nano-structured shell. The shell operates as a metamaterial-based impedance matching interface between the input light and a photonic jet and, at the same time, forms the material basis for the nonlinear wavelength conversion. We have adopted variants of the ‘hedgehog’ particles, which comprise an array of high-aspect ratio ZnO nano-spikes arranged orthogonally onto a silica microscope of 1 mm in diameter. The sub-wavelength arrangement of these nano-spikes forms a spherical metamaterial shell exhibiting a radically graded effective index. Such a configuration effectively confines the incident light into a strong photonic jet within the shell, which is made of a well-known ε0/3 material, thereby significantly enhancing the SHG signal compared to a flat array of similar nano-spikes. In addition, due to the non-resonant nature of the nonlinear conversion, following advantages are further conceived: 1) relaxation of the geometrical constraints in the construction of the metamaterial shell, 2) broadband wavelength tuning, 3) lower sensitivity to angle of incidence and polarization and 4) directional scattering of the SHG signal. We have experimentally observed strong enhancements of SHG in a variety of ‘hedgehog’ particles. Through the FDTD simulations, we observed strong enhancement of the SHG conversion efficiency in ‘hedgehog’ particles having 300 ZnO nanospikes whose geometrical features do not coincide within the resonant conditions. The simulations revealed 6×10^8-fold enhancement in the SHG efficiency compared to a single ZnO spike. The demonstrated concept of enhanced light to heat and enable highly specific drug delivery combining photothermal therapy with chemo and immunotherapy for enhanced treatment outcome in highly aggressive breast cancer.

8:00 AM *EP12.06.01
Exciton-Plasmon Coupling at Plasmonic Surfaces and Implications for Thin-Film Optoelectronics Deirdre O’Carroll1, 2, 3; 1Materials Science and Engineering, Rutgers University, Piscataway, New Jersey, United States; 2Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey, United States; 3School of Physics, Trinity College Dublin, Dublin, Ireland.

Excitonic semiconductor thin films are emerging as next-generation active layer materials in optoelectronic devices used for display, solid-state lighting, laser and energy harvesting applications. However, active layer thicknesses in these devices are typically limited to 200 nm or less due to limited charge carrier diffusion lengths in excitonic semiconductor materials. Therefore, light management and localization in excitonic semiconductor thin films requires manipulation of light below the diffraction limit. As a result, to improve energy conversion efficiency in excitonic semiconductors, light manipulation using plasmonic structures integrated with the thin film excitonic material is of interest.

Here, our work on improving light trapping, light extraction and stimulated emission in excitonic organic semiconductor thin films using a variety of plasmonic metasurfaces will be presented. Numerous optical phenomena, such as absorption induced scattering, out-of-plane waveguiding and morphology-dependent surface plasmon outcoupling, are identified due to exciton-plasmon coupling between the organic semiconductor and the plasmonic metasurface. Interactions between localized and propagating surface plasmon polaritons and the excitonic transitions of a variety of organic conjugated polymer materials will be discussed and ways in which these interactions may be optimized for particular optoelectronic applications will be presented. Furthermore, our recent studies on the impact of exciton-plasmon coupling on stimulated emission from thin-film spasers will be presented.

8:30 AM EP12.06.02
Large Area Asymmetric Plasmonic Crystals Fabricated via Nanoimprint Lithography and Tilted Angle Metal Deposition Cristiano Matriardi, Juan Luis Garcia-Pomar, Maria Isabel Alonso and Agustín Mihí; Nanostructured Materials for Optoelectronics and Energy, Instituto de Ciencia de Materiales de Barcelona, Bellaterra, Spain.

Asymmetric and chiral plasmonic nanostructures have been widely used in the past to study the evolution of chirality as a function of geometrical parameters1, 2, 3. In particular, ordered arrays of asymmetric nanostructures can be designed to allow the interaction of surface plasmon polaritons (SPPs) with localized surface plasmons (LSPs) and increase the chiroptical effect4, 5. These emerging plasmonic architectures are pushing the limit of nanofabrication toward new approaches, such as multi-step e-beam lithography4 and colloidal nanohole lithography5. However, the development of low-cost, high throughput and large-area manufacturing techniques still remain a challenge in this field, especially for systems working at optical wavelengths.

We present a straightforward method to produce large area asymmetric plasmonic crystals with a sub-micrometer periodicity that shows intense polarization dependent resonant modes at optical wavelengths. Full control of the geometry allows us to fabricate different structures with gradual loss of symmetry along the 3D axis. The core fabrication process involves a first soft-lithographic nanoimprinting of photocurable resist followed by tilted metal deposition. Concretely, samples with a square array of holes with a pitch length of 500 nm were mounted on a tilted sample holder (0°, 20°, 45°). At a glancing angle, silver was deposited onto the pattern resulting in arrays of asymmetric plasmonic nanostructures. Reflectivity measurements, together with FDTD numerical simulations, unveil the degeneration of resonant modes due to the loss of symmetry and allow us to understand the physics underlying them. We demonstrate fine tunability of the resonant modes and polarization dependent photoluminescent enhancement of organic dyes.

References
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5) B. Frank, X. Yin, M. Schäferling, J. Zhao, S. M. Hein, P. V. Braun, and H. Giessen ACS Nano 2013 7 (7), 6321-6329

4:30 PM *EP12.05.07
Cancer Diagnosis and Response to Treatment with Plasmonic Nanoprobes Rizia Bardhan; Vanderbilt University, Nashville, Tennessee, United States.

In the past two decades, plasmonic nanostructures have gained tremendous interest as both diagnostic and therapeutic agents for cancer detection and treatment. In this talk I will show the utility of gold nanostar probes designed in my lab for rapid and noninvasive detection of multiple immunomarkers of cancer to enable patient selection for immunotherapies, as well as response to treatment after immunotherapy. We combined a clinical and pre-clinical imaging technique, positron emission tomography with surface-enhanced Raman spectroscopy (ImmunoPET-SERS) in vivo by labeling gold nanostars with radiolabels, Raman reporter molecules, and targeting antibodies. Multimodal ImmunoPET-SERS seamlessly integrates depth-resolved whole-body imaging and high sensitivity of PET with high spatiotemporal resolution and multiplexing of SERS providing dynamic immunomarker profiling in vivo. Further, we determined the immunomarker status of mice treated with combinatorial immunotherapy with ImmunoPET-SERS and demonstrated real-time feedback of CD8+ infiltration in tumors which was confirmed with IHC. Enhanced Raman spectroscopy (ImmunoPET-SERS) exhibits a radially graded effective index. Such a configuration effectively confines the incident light into a strong photonic jet within the shell, which is made of a well-known ε0/3 material, thereby significantly enhancing the SHG signal compared to a flat array of similar nano-spikes. In addition, due to the non-resonant nature of the nonlinear conversion, following advantages are further conceived: 1) relaxation of the geometrical constraints in the construction of the metamaterial shell, 2) broadband wavelength tuning, 3) lower sensitivity to angle of incidence and polarization and 4) directional scattering of the SHG signal. We have experimentally observed strong enhancements of SHG in a variety of ‘hedgehog’ particles. Through the FDTD simulations, we observed strong enhancement of the SHG conversion efficiency in ‘hedgehog’ particles having 300 ZnO nanospikes whose geometrical features do not coincide within the resonant conditions. The simulations revealed 6×10^8-fold enhancement in the SHG efficiency compared to a single ZnO spike. The demonstrated concept of enhanced light to heat and enable highly specific drug delivery combining photothermal therapy with chemo and immunotherapy for enhanced treatment outcome in highly aggressive breast cancer.

SESSION EP12.06: Photonics
Session Chairs: Fang Liu and Alexey Nikitin
Thursday Morning, April 25, 2019
PCC North, 200 Level, Room 226 A
Metamaterials and Metasurfaces for Narrowband Rejection Filters

9:00 AM

Polycrystalline VN, NbN and TaN films and their plasmonic performance. In a final effort to generalize these results we extend this study to point defects have more crucial consequences to the plasmonic performance of TiN than the extended defects; as a result, an effective strategy to grow efficient plasmonic TiN is to use intense irradiation conditions that anneal the point defects out of the grains, albeit in expense of grain size. In a final effort to generalize these results we extend this study to polycrystalline VN, NbN and TaN films and their plasmonic performance.

We show that relying exclusively on XRD for the evaluation of crystalline quality of TiN may be misleading. Indeed, the combined XRD-XPS-Raman results clearly show that the Fermi level that trap electrons and enhance the dielectric losses, as shown by previous ab initio calculations. For some conductive nitrides, like TaN, MoN and WN, point defects were reported to form spontaneously as a mechanism of stabilization of epitaxial films. In order to identify the effects of point and extended defects we provide a detailed study of the optical properties and plasmonic behavior of a wide range of polycrystalline and heteroepitaxial TiN films as measured by ellipsometry in the broadband range of 190-40000 nm. These films have varying crystallographic features and chemical composition and were grown by reactive magnetron sputtering at various temperatures and irradiation conditions. The crystallographic features are studied by X-Ray diffraction (XRD) at various geometries (Bragg-Brentano, Phi-scans, Rocking Curves), the chemical composition by X-Ray Photoelectron Spectroscopy (XPS) core level spectra, the point defects by Raman spectroscopy, and the electron density of states (EDOS) by valence band XPS spectra. We show that relying exclusively on XRD for the evaluation of crystalline quality of TiN may be misleading. Indeed, the combined XRD-XPS-Raman results clearly show that the point defects have more crucial consequences to the plasmonic performance of TiN than the extended defects; as a result, an effective strategy to grow efficient plasmonic TiN is to use intense irradiation conditions that anneal the point defects out of the grains, albeit in expense of grain size. In a final effort to generalize these results we extend this study to polycrystalline VN, NbN and TaN films and their plasmonic performance.

9:30 AM

Hybridized Plasmonic Gap Mode in Gold Nanorod on Mirror NANOantenna for Spectrally Tailored Emission Enhancement

Hiroshi Sugimoto and Minoru Fujii; Kobe University, Nada Kobe, Japan.

Plasmonic nanoantenna offers the ultimate spatial control over electromagnetic waves by localizing the optical energy in the nanoscale and has significant potential for the nanophotonic applications utilizing enhanced light matter interactions. A nanogap structure in particular have an extremely small mode volume and a large field enhancement and a resultant large Purcell factor. However, formation of a sub-10 nm gap with an accuracy of ~1 nm is still challenging even by the state-of-the-art lithography techniques. Recently, plasmonic nanoparticle on mirror antennas in which a metal nanoparticle (NP) is placed on a metal film via dielectric spacer have shown the great potential in nanophotonic applications.[1,2] The structure can be fabricated by a bottom-up process using colloidal gold and silver NPs with a sub-10 nm gap. However, in spherical NP on mirror structure being studied experimentally, the degree of freedom of the antennas in terms of spectral and polarization control is limited. In this work, we report spectral shaping and polarization control of Purcell-enhanced fluorescence by the gap plasmon modes of an anisotropic gold (Au) nanorod on a mirror (NRoM) antenna.[3] We first simulate the property of the resonant modes under different excitation conditions. Systematic calculations demonstrate the richer resonance behaviors of a NRoM antenna than a spherical NPoM antenna due to the hybridization of the bright and dark modes driven by the structural anisotropy. We fabricate a NRoM antenna by placing a Au NR on an ultra-flat Au film via a mono- and multi-layers of light emitting quantum dots (QDs) (~3 nm in diameter). The experimentally measured resonance spectra of single NRoM antennas agree quite well with those of the numerical simulations. We demonstrate large enhancement (~900-fold) and shaping of the luminescence spectrum from QDs in the gap due to the coupling with the hybridized mode of a NRoM antenna. We also show that the polarization property of the emission is controlled by that of the mode coupled. These findings provide novel insights for the design of spectroscopy-based sensing and imaging at the single nanometer scale using the nanoantenna-enhanced emission enabled by hybridized plasmonic modes.


9:45 AM

Atomically- Thin Tunable Exciton Lens

Jorik Van de Groep, Jung-Hwan Song and Mark L. Brongersma; Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California, United States.

Since the development of diffractive optical elements in the 1970s research has focused on replacing bulky optical elements such as lenses and gratings by thin counterparts. Over the last decade, nanoepitaxial metasurfaces rapidly advanced the development of flat optical elements based on the realization that resonant optical antenna elements enable local phase control. Present applications of metasurface flat optical elements include lenses, polarization control, and beam steering.

Next-generation applications of flat optics require dynamic control over optical functionalities, e.g. the focal position or efficiency of optical elements. However, most nanoepitaxial structures are static after design and fabrication. Current approaches for dynamic control like electrical gating exhibit limited tunability due to the finite few-nm extent of the depletion and accumulation layers as result of coulombic screening.

Here, we demonstrate actively-tunable and atomically-thin optical lenses by carving them directly out of monolayer transition-metal dichalcogenides (TMDs) like WS2 with a strong excitonic resonance in the visible spectral range. This turns the 2D material into the antenna or metamat material and incorporation of active materials into larger antenna structures will no longer be needed. Due to their sub-nm thickness, these materials are highly tunable through external control. We demonstrate dynamic electrical tuning of the focusing efficiency through manipulating of the excitonic material resonance properties as opposed to tuning of antenna resonances.

10:00 AM BREAK

10:30 AM

Metamaterial Absorber with Nanofluidic Channel for Attomole Nanoconfined Molecular Detection

Takuo Tanaka,1,2,3,4 Metamaterials Laboratory, RIKEN Cluster for Pioneering Research, Wako, Japan; 1Innovative Photon Manipulation Research Team, RIKEN Center for Advanced Photonics, Wako, Japan; 2School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Japan.

In bioanalysis, especially in single cell analysis, label-free detections and recognitions for molecular analysis are highly demanded. IR spectroscopy is one of label-free methods and it gives us chemical specificity and molecular information, yet its application in bioanalysis is limited due to its low sensitivity. Recently, plasmonic nanostructures were intensively studied to improve the sensitivity of IR spectroscopy by several orders of magnitude, however positioning analytes exactly at the hot-spots is still challenging [1]. We propose a device that utilizes nanofluidics to manipulate analytes into the hot-spots of metamaterials, consequently an ultra-high sensitivity of IR absorption detection can be achieved.

The structure consists of metal square-disks array and metal mirror separated by a nano fluidic channel. The interaction between top square nanostructure and bottom mirror forms the quadruple resonance, and it suppresses the light reflection from the device. When the molecule whose absorption is overlapped with this mode is introduced, strong interaction between molecules and metamaterials is excited and it creates the reflection light within the absorption band of the metamaterial. The sensitivity was achieved at molecule density of ~10⁴ molecules/Å², which is improved by 2 orders compared to reported plasmonic induced IR detection methods [2]. We also succeeded in the quantitative determination of absolute number of molecules by precise fluidic operation. Moreover, the device allows the confinement of both molecules and plasmonic energy inside the nanocavities. We confirmed the presence of a strong H-bond network and the
scaling behavior of water confined in 10-100 nm regime. Our method can provide the capability for in-situ probing molecules and chemical reactions under nanoconfinement [3]. When we make the size of unit cell of metamaterial absorber down to several hundreds nanometers, the absorption bands move to the visible light region. We present a simple yet efficient approach for ink-free color printing employing sub-micrometer scale plasmonic pixels of single constituent metal structure that supports near unity broadband light absorption at two distinct wavelengths, facilitating the creation of saturated colors [4]. The dependence of these resonances on two different parameters of the same pixel enables controllable color attributes such as hue, brightness and saturation across the visible spectrum. Here we present an up scalable color printing scheme using plasmonic pixels of single constituent metal structure, enabling the design of full colors with controllable color attributes.


11:00 AM EP12.06.08

Ultra-Flat, Transparent and Rainbow-Free Guided Mode Resonance for Diffractive Optical Eye Tracking Glass

Jung-Hwan Song, Jorik Van de Groep and Mark L. Brongersma; Stanford University, Stanford, California, United States.

Over several decades, eye tracking has been providing indispensable analysis tool in wide range of research fields including Ophthalmology, Psychology, and Neurology. Recently, augmented reality is pushing its demands on more compact, transparent optical eye trackers, which are compatible to head-mounted display or heads-up display. The requirement augmented reality imposes on the optical eye trackers is tracking human eyes while it does not perturb human vision. The optical eye trackers should have acceptable power efficiency as well as maintain optical transparency. The two requirements—power efficiency and high-transparency to human vision—are typically conflict to each other.

Many of proposed optical eye tracking systems, such as oblique half-mirror and holographic waveguide are suffering from either severe human vision interference or poor operation efficiency. In addition, these are bulky, poorly transparent, and producing rainbow images due to non-zero diffraction in the visible spectrum. Here, we demonstrate ultra-flat, transparent, and rainbow-free diffractive eye tracking glass based on guided mode resonance which supports near-unity transmission. It is based on a 200-nm-thick SiNx slab dielectric optical waveguide between a quartz substrate and a 100-nm-thick SiO2 capping layer. The vertical feature is designed for high transmission (>90%) over the whole visible spectrum. We insert 3-mm-thick Si grating layer between the SiNx slab dielectric waveguide and SiO2 capping layer which launches high-quality (Q=2,000) guided mode resonances in the slab waveguide. We rigorously characterize the resonantly diffractive, dispersive properties of the fabricated structures through angle-resolved confocal spectroscopy. The guided mode resonance is excited when light of resonant wavelength (870 nm) in near-infrared spectrum is normally incident on the structure. The scattered light components at individual the Si gratings constructively interfere to be fanned into quasi-guided waves in the SiNx slab dielectric waveguide. During long (2,000 optical cycles) travelling time inside the SiNx slab before re-radiation into the free space, the light is building up its intensity and coming out with high diffraction efficiency (13%) into the desired direction which is useful for eye tracking. When the incident light is in the visible spectrum, on the other hand, the guided mode resonance becomes weak due to Si absorption, resulting in suppressed rainbow-producing diffractions with negligible (0.1%) efficiency. We also demonstrate the imaging of artificial eye by a single webcam located at the 60 degree from the surface-normal direction of fabricated 2 cm by 2 cm sample. The full anterior images of an artificial eye are obtained at the oblique direction and we hope that this opens a promising route toward ultra-compact, transparent, and non-obtrusive imaging for displays and optical switching applications.

11:15 AM EP12.06.09

Active Tuning of Plasmons and Surface-Phonon Polariton Resonances

Adam Dunkelberger1, Chase Ellis1, Daniel Ratchford1, Alexander Giles1, Scott Katzer1, Roderick Davidson1, Andrea Grafton1,2, Mijin Kim1, Chul Soo Kim1, Igor Vurgaftman1, Joseph Tischler1, Joshua Caldwell2 and Jeffrey C. Owstsky3; 1U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2NRC/RAP Postdoctoral Fellow, Washington, District of Columbia, United States; 3KeyW, Inc., Hanover, Maryland, United States; 4Vanderbilt University, Nashville, Tennessee, United States.

The infrared spectra of many polar semiconductors are dominated by highly reflective reststrahlen bands that occur between the transverse and longitudinal optical phonons. We have previously shown that photoinjected carriers transiently and reversibly modify the reststrahlen bands through carrier-induced charge modulation. Here, we report on the active control of the reststrahlen bands in high-quality SiGe/SiGeI strained-layer optical structures using a surface-phonon polariton (SPP) resonant cavity. We use time-resolved infrared reflection spectroscopy to identify the frequency tuning of the SPP resonance in the presence of photoexcited carriers, with electro-optical measurement of the change in cavity permittivity. The active control of the SPP resonance is demonstrated for SiGe/SiGeI strained-layer mirror cavities using a range of optical materials and device structures, including high-quality strained-layer mirrors. The results demonstrate the potential for active control of SPP resonances in a variety of device applications, including optical frequency conversion, optical phase conjugation, and optical switching.

11:30 AM *EP12.06.10

Thin Films andMetasurfaces for Optical Information Processing

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Extraction of the properties of optical wavefields, such as wavelength, polarization and phase, is widely employed in a range of applications including optical communications, sensing and imaging. These attributes of light are, however, not directly sensed by photodetectors and additional optical components or computational post-processing of intensity images is required to extract this information. Similarly, optical information processing is widely used for enhancing images and the visualization of transparent objects such as live unstained cells. Various well-known computational and all-optical strategies have also been developed to perform image manipulation. To sense properties of light other than its amplitude or to selectively modify optical images, therefore, either real-time approaches requiring bulky and expensive optical components, or methods utilizing potentially time-consuming computational strategies are employed. Here we discuss the use of plasmonic thin films and metasurfaces to directly convert amplitude and phase gradient information in an optical field into enhanced intensity images and the incorporation of plasmonic antennas into photodetectors to sense polarization, phase gradients and color. These devices provide an avenue for the development of ultra-compact systems that will perform on-chip, real-time, single-shot conversion of wavefield information to readily measured and enhanced intensity distributions or a measurable photocurrent.

There have been several recent demonstrations of the use of metasurfaces and plasmonic thin films to perform mathematical operations. For example, a metasurface can be used as a tailorable spatial filter in a conventional optical spatial filtering system where optical differentiation or integration can be performed using independent tuning of the amplitude and phase of scattered light at different spatial locations on the filter. Alternatively, and the method to be discussed here, the angular sensitivity of certain plasmonic resonances permits direct access to the Fourier (or angular) spectrum of a reflected or transmitted field establishing the possibility of ultra-compact approaches to optical information processing. The angular dependence of prism coupling to surface plasmons on a thin metal has been previously used to demonstrate differentiation of images both amplitude and phase. Here we will discuss the use of<br>

2:00 PM EP12.07.02 Effects of Nanostructured Plasmonic Environment on Electrochromic Polymer Switching Mohammad Shahabuddin, Carl Bonner, Natalia Noginova and Sohelia Mashhadi; Center for Materials Research, Norfolk State University, Norfolk, Virginia, United States.

Strong modification of local environment associated with plasmonic nanostructures provides possibilities to control various processes, including charge transfer processes and chemical reactions. In this work, we explore opportunities to enhance electrochromic polymer performance using plasmonic metamaterials, and study the origin of this enhancement. Electrochromic polyaniline (PANI) films deposited onto gold metasurfaces demonstrate non-monotonous coloration behavior at low voltages, step-like color-change and much faster saturation in color change compared with polyaniline films deposited on flat gold. The additional small voltage peak in the cyclic voltammogram in nanomesh/PANI cell and the asymmetric and nonlinear I-V characteristics of the sandwich nanomesh/PANI/flat gold structure indicate a possible formation of Schottky-like interface between polyaniline and nanogold structured, whereas the Ohmic contact is observed for the flat gold-polyaniline system. The results are discussed in terms of the modified work-function of nanogold structured, interface charging and threshold-like charge transport. Possibility to engineer optical and charge transport properties of electrochromic materials via nanostructured interfaces can bring various optoelectronic applications.

2:15 PM EP12.07.03 Enhanced Reflection at Glancing Angles from a Pt/SiN Metamaterial Perfect Absorber Nicole Pfister and Thomas E. Vandervelde; Tufts University, Medford, Massachusetts, United States.

Many metamaterial devices are designed to operate at a wide range of angles of incidence. However, the ability to control reflection at an angle is useful for 3-D imaging and detection, as well as controlling light for photonic circuits. We have demonstrated a metal-dielectric-metal metamaterial perfect absorber that can be either angle-dependent or angle-independent based on the dielectric material chosen for the spacer layer. Use of platinum and silicon nitride produced increased selectivity of the near infrared perfect absorber at wide angles of incidence under p-polarized light. This enhanced selectivity came from increased reflection at wavelengths smaller than the target wavelength for absorption.

Variable angle spectroscopic ellipsometry was used to explore the enhanced reflection. Based on the Mueller matrix, the sample exhibited a small amount of anisotropy, though to what degree depended on the angle of incidence and orientation of the sample. When the long elliptical axis was perpendicular to the plane of incidence, the sample appeared more anisotropic, particularly at wider angles of incidence. Depolarization and scattering measurements showed that the anomalous behavior is not a function of scattering or cross-polarization, indicating that a resonant mode within the metamaterial is being induced. FEM simulations confirmed that anti-parallel electric field curls are only present in the cases where enhanced reflection occurs, generating a magnetic dipole that contributes to the metamaterial’s response. To determine if this behavior is specific to this combination of materials and device design, additional simulations were conducting with varying material parameters and ellipsoidal axes.

To explore the design space where the enhanced reflection occurs, the permittivity of the dielectric layer and the long elliptical axis were varied. From these simulations, three regions appeared. The first, with high permittivities and long elliptical axes near the size of the unit cell, showed angles of incidence independent behavior with no enhanced reflection, which was consistent with devices found in literature. The second region, where the nanostructure approached a circle as the elliptical axes became equal and the permittivity of the low, showed extreme increasing in reflection, though with losses to the designed absorption peak. In this region, many designs did not exhibit a metamaterial response at all as the permittivity of the dielectric layer was too low to support the resonant modes.

Finally, in region three, a range of permittivity values and elliptical column sizes resulted in the reported enhanced reflection but with high levels of absorption at the target wavelength. Therefore, this behavior is more common than previously thought. Obtaining a thorough understanding of the design space like this will lead to better informed device decisions for other applications.

2:30 PM EP12.07.04 Plasmonic Nanovoids in Silicon—Simulation and Experiment Hanna Bandarenka1, Sergey Redko2, Aliaksand Shapel1, Aliaksa Shkarshniou1, Stanislau Niauzorau1 and Bruno Azeredo2; 1 Applied Plasmonics Laboratory, Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus; 2 Laboratory of Materials and Structures of Nanoelectronics, Belarusian State University of Informatics and Radioelectronics, Minsk, Belarus; 3 The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, Arizona, United States.

Ordered arrays of plasmonic nanovoids (antinanoparticles) provide unconventional plasmonic platforms for detection and study of organic molecules at ultralow concentrations by surface enhanced Raman scattering (SERS) spectroscopy. They are especially attractive for analysis of large molecules that cannot be objectively studied with traditional plasmonic nanoparticle. This is caused by the small areas of localization of electromagnetic field (hot spots) that is induced by surface plasmon resonance in nanoparticles. As a result, Raman signal from particular bonds of large molecules, which are located beyond hot spots, is not enhanced. Electromagnetic field of nanovoids is mostly localized inside cavities due to multiple bounces of excitation light. If an analyte molecule appears in nanovoid, Raman signal of all bonds will be increased nearly equally. To promote significant enhancement plasmonic nanovoids should have depth and diameter more than 0.5 microns. Such structures are usually fabricated by nanosphere lithography, which main drawbacks are (i) limited area of plasmonic sample and (ii) high consumption of noble metals. Here we propose to fabricate plasmonic nanovoids by sculpturing the silicon template and following electrochemical/electroless deposition of silver film. Arrays of voids with proper dimensions in silicon can be fabricated by electrochemical anodic etching [1] or direct electrochemical imprinting with dotted stamp [2]. Using the first approach, we were able to form arrays of macropores in lightly doped p-type silicon, which have sizes deviating from 0.5 to 1.5 microns and slightly variable profile causing partial non-repeatability of the substrate’s optical and electromagnetic properties. On the other hand, the second method leads to etching the voids with well-reproducible periodical structure and related properties. Effectiveness of nanovoids was estimated by simulation of electric field distribution under different excitation wavelengths for the cavity in silicon coated with continuous silver film with 100 nm thickness. The distance between nanovoids was 10 nm. The depth and diameter of simulated nanovoids were 0.5 microns. We solved a 3D frequency-domain wave equation for electric field with a finite element method (FEM). To simulate the excitation light we used a plane wave with a normal incidence. Simulations showed electric field enhancement in the void volume due to internal reflections. It was found that the electric field in nanovoids is 2-3 orders of magnitude higher than the field in the silicon slab. The maximal electric field shifts from the bottom to the mouth of nanovoid according to increase of excitation wavelength from 473 to 980 nm. Localization of electric field maximum in the center of nanovoid was typical for 785 nm. Experimental SERS measurements of peptides and proteins at micromolar concentration showed that the most number (80%) of full-view spectra were obtained at 785 nm. Considering simulation results this can be explained by uniform overlapping the analyte molecules with the centered electric field. In future work, fabrication of films of other metals and optimization of their deposition process on the template formed by direct electrochemical imprinting with stamp is needed. This would enable to analyze large molecules at lower concentrations and achieve reproducibility of their SERS-spectra for 90 – 95% of nanovoids.


2:45 PM EP12.07.05 Compact a-Si Nanopillar Arrays for Spectral Filtering via Guided Mode Resonances Ryan C. Ngi1, Julia Green2 and Katherine T. Fountaine3; 1 California Institute of Technology, Pasadena, California, United States; 2 NGI Next, Northrop Grumman Corporation, Redondo Beach, California, United States.
Sub-wavelength periodic structures have potential in many various applications due to their unique spectral characteristics. These arrays exhibit near-unity reflectivity resonances that arise from the coupling of an incident wave into a leaky waveguide mode via a grating vector that is subsequently re-radiated, a phenomenon commonly known as a guided mode resonance (GMR). Such spectral characteristics are well-suited for multi- and hyper-spectral filtering applications in the infrared. We designed an all-dielectric platform consisting of amorphous silicon (a-Si) (n \approx 3.5) nanopillar arrays embedded in SiO_{2} (n \approx 1.4) with a ratio of radius, r, and a center-to-center distance, d, of r/d \approx 0.2 in simulation and experiment for application as narrow stopband filters. These filters are ultra-thin (<0.1μ), polarization-independent, relatively straightforward to fabricate compared to conventional Bragg stack reflectors, and possess greater efficiencies relative to their plasmonic-based counterparts due to low material absorption. The choice of a-Si as the nanopillar material stems from its low cost, high index of refraction, and a band gap of 1.55 eV near the edge of the visible.

We present the tunability of the spectral characteristics of the GMR in these arrays through variation of array geometric parameters in simulation and experiment and validate the GMR formulation with photonic crystal slab band diagram calculations. The GMRs are observed experimentally in fabricated arrays with an amplitude >85% with FWHM values ranging from 20-50 nm. We further extend our analysis to periodic arrays of finite size, which are required for high resolution snapshot imaging. GMR designs often consider only the case of an infinite array, where the leaky waveguide mode can propagate laterally for hundreds of periods, allowing for this mode to eventually scatter out of the array giving rise to the characteristic narrow near-unity rapid spectral variations of a GMR. With an insufficient number of periods, the quality factor and thus the optical filtering performance is greatly diminished. We present arrays that operate under finite size limitations optimized for spectral imaging applications in the near-infrared.

3:00 PM BREAK

3:30 PM *EP12.07.06 On-Chip Free Electron Light Source Fang Liu1,2; Tsinghua University, Beijing, China; 2Beijing National Research Center for Information Science and Technology, Beijing, China.

To generate Cherenkov radiation (CR) in natural medium, the electron energy threshold is higher than hundreds of keV. Even though various approaches were adopted, the high-energy electrons as high as tens of keV is still required in experiment. Here we proposed to eliminate the threshold of electron energy to generate CR with the help of hyperbolic metamaterial (HMM). The analytical and simulation results indicate that, even though electron energy is lower than 0.1keV, the CR could be obtained in HMM in a visible and near-infrared frequency region. Furthermore, the on-chip integrated threshold-less CR source has been realized. It is demonstrated that the electron energy generating CR experimentally is two-three orders of magnitude lower than that in natural medium and the first on-chip integrated free electron light source is realized. Moreover, having free electrons interact with surface plasmon polariton (SPP) cavity mode, the surface plasmon amplification by stimulated emission of radiation (SPASER) is discovered and used for realizing lasers at nanometer scale. The conventional gain media applied in SPASER are solid materials such as organic dye or semiconductor, which limits the frequency range of SPASER. Actually, the free electrons could be considered as a kind of gain medium for emitting radiation. Here, we investigate theoretically the SPASER excited by free electrons and demonstrate numerically the tunable, deep-ultraviolet, and ultracompact laser by having free electrons interact with surface plasmon polariton mode supported on metal surface. The wavelength in deep ultraviolet could be widely tuned by varying the electron energy. Our work opens up the possibility of exploring high performance on-chip integrated free electron light source and optoelectronic devices, and provides a way for realizing integrated free electron laser in ultraviolet frequency region.

4:00 PM EP12.07.07 Coupling of Boron Dipyromethene Dye Excitons to Plasmonic Surface Lattice Resonances in Aluminum Nanodisk Arrays Robert Collison1, Jacob Trevino2, Vinod Menon2 and O’Brien Stephen3; 1The Graduate Center, CUNY, New York, New York, United States; 2Chemeloon Inc., New York, New York, United States; 3City University of New York, New York, New York, United States.

When plasmonic metal nanoparticles are arranged in extended, one- or two-dimensional periodic arrays, the localized surface plasmon resonances (LSPRs) of the individual particles will couple radiatively to form a collective, propagating photonic-plasmonic mode known as a surface lattice resonance (SLR). Currently, SLRs and their potential applications in photonic devices, such as solar cells and light-emitting diodes, are growing topics of interest in the literature. In particular, the interaction of propagating, delocalized SLRs with the highly localized excitons of organic dye molecules is being investigated, and exotic phenomena such as the Bose-Einstein condensation of polaritons composed of dye excitons coupled to SLRs was recently reported. We report on the fabrication of SLR-supporting arrays of aluminum nanodisks on glass, and the coupling of these SLRs to dye excitons via coating of the arrays with dye-doped poly(methyl methacrylate). In particular, the interaction of the SLRs with boron dipyromethene (BODIPY) dye is examined, and the resulting effects, including angle-dependent fluorescent emission and enhancement of energy transfer between two different BODIPY dyes, are reported.


4:15 PM EP12.07.08 Tailoring UV Circular Dichroism with Semiconducting Metamaterials Sunam Sarkar and John Gibbs; Northern Arizona University, Flagstaff, Arizona, United States.

Chiral electromagnetic metamaterials that have chiroptical activity, have attracted attention due to their suitability for many potential photonic and biological applications including lasers, molecular sensing, structural studies of organic molecules such as proteins and DNA. Despite the recent advances in chiral metamaterials, to date, very little attention has focused upon artificially large optical activity in the UV range, where molecular circular dichroism (CD) bands are most frequently encountered. In this work, a systematic investigation is made into CD behavior in the UV range with respect to geometry and critical dimensions with a semiconducting metamaterial. The glancing angle deposition (GLAD) method was used as it provides a means of experimentally investigating the relationship between morphology and optical activity, which is critical to optimizing design. We also explore more complex, multi-material and multi-functional hybrid metamaterials that are active across the UV and visible spectrum. This technique allows us to tailor optical activity making it possible to achieve chiroptical activity over a wider range of wavelengths.

4:30 PM EP12.07.09 Leveraging Momentum to Dictate Spectral Tuning of Infrared Phonon-Polaritonic Thomas Beechem1, Christopher Saltonstall1, Tristan Gilbert2, Joseph Matson2, Fabian Ugwu3, Rachel Kasica3, Francisco Bezare3, Jason Valentine4 and Joshua Caldwell2; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Vanderbilt University, Nashville, Tennessee, United States; 3National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 4University of Puerto Rico, Cayey, Puerto Rico, United States.

The nanophotonics field has long sought to identify mechanisms to realize dynamical control of optical modes. In most approaches, the magnitude of tuning is dependent upon the multi- and hyper-spectral filtering applications in the infrared. We designed an all-dielectric platform consisting of amorphous silicon (a-Si) (n \approx 3.5) nanopillar arrays embedded in SiO_{2} (n \approx 1.4) with a ratio of radius, r, and a center-to-center distance, d, of r/d \approx 0.2 in simulation and experiment for application as narrow stopband filters. These filters are ultra-thin (<0.1μ), polarization-independent, relatively straightforward to fabricate compared to conventional Bragg stack reflectors, and possess greater efficiencies relative to their plasmonic-based counterparts due to low material absorption. The choice of a-Si as the nanopillar material stems from its low cost, high index of refraction, and a band gap of 1.55 eV near the edge of the visible.

We present the tunability of the spectral characteristics of the GMR in these arrays through variation of array geometric parameters in simulation and experiment and validate the GMR formulation with photonic crystal slab band diagram calculations. The GMRs are observed experimentally in fabricated arrays with an amplitude >85% with FWHM values ranging from 20-50 nm. We further extend our analysis to periodic arrays of finite size, which are required for high resolution snapshot imaging. GMR designs often consider only the case of an infinite array, where the leaky waveguide mode can propagate laterally for hundreds of periods, allowing for this mode to eventually scatter out of the array giving rise to the characteristic narrow near-unity rapid spectral variations of a GMR. With an insufficient number of periods, the quality factor and thus the optical filtering performance is greatly diminished. We present arrays that operate under finite size limitations optimized for spectral imaging applications in the near-infrared.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.
Plasmonic nanostructures have gained prominence thanks to their ability to confine electromagnetic fields far below the wavelength. By virtue of the collective resonant oscillations of free electrons in metallic structures, extremely high field enhancements can be achieved [1]. These resonances are strongly related to the shape, size as well as the material properties of the nanostructures. While till date, in most cases, the spectral properties have been determined by the shape and size, the ability to tune the material properties, provides additional advantages and offers a new degree of freedom for designing plasmonic nanostructures. Alloying is an attractive way of tuning the properties of metals since it alters the permittivity and, consequently, changes the resonance wavelength [2]. In our work, we employed gold and silver alloys (Au/Ag alloy) of different composition to fabricate nanostructures of different shapes and sizes including complex structures exhibiting Fano resonances. To this end, a very original low-temperature process has been developed, which allows the nanostructures to retain their shape.

Our work aims to fabricate alloyed plasmonic nanostructures using standard techniques of e-beam lithography and lift-off. We deposit consecutive metal layers, where the thickness, hence the volume, of each layer determines the desired composition, using e-beam evaporation technique, in contrast, to often used co-sputtering [4]. Here, we demonstrate the performance of a newly developed low-temperature annealing process using three different Au/Ag alloys, namely, Au0.2Ag0.8, Au0.5Ag0.5, and Au0.8Ag0.2. A uniform alloy is achieved by annealing the previously deposited metal layers at temperatures of 300°C for 8 h and 450°C for 30 mins under N2 atmosphere. The experiments reveal that using such low temperatures, far below the Tammann temperature, at which the mobility of the molecules in a solid sets in, the shape of the nanostructures are perfectly conserved! EDX and XPS measurements carried out on 150 nm thin films of the Au/Ag alloys confirm a homogeneous alloy. Ellipsometric studies carried out on thin films confirm further that the permittivity of alloys can be tuned. After successful fabrication of alloyed thin films, 50 nm high equilateral nanotriangles of 300 nm side length and nanorods of 400 nm and 50 nm length and width, respectively, and periodicity of 4 μm were fabricated by e-beam lithography. Shape and size of the structures are perfectly retained after annealing and EDX measurements confirm fully homogeneous alloys. We also fabricated more complex Au/Ag Fano-resonant plasmonic nanostructures using this technique. The optical response of a 4 rod Fano resonant structure excited with light polarised along its long axis [4] has been simulated for five different compositions, namely, pure Ag, Au0.2Ag0.8, Au0.5Ag0.5, and Au0.8Ag0.2, and pure Au. The simulations clearly show a variation of the spectrum by altering the composition. These nanostructures were successfully fabricated, and experimental spectra confirmed the variation of resonances by varying the composition.

To conclude, we successfully demonstrated a novel fabrication technique where plasmonic nanostructures of different shapes and compositions retain their shape after low-temperature annealing of consecutively deposited Au and Ag layers. This result opens up the opportunity of fabricating plasmonic nanostructures of different material compositions, which offers a new degree of freedom for tailoring the optical properties of plasmonic nanostructures.

References

SYMPOSIUM EP13

Thermoelectrics—Materials, Methods and Devices
April 23 - April 26, 2019

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SESSION EP13.01: Advances in Thermoelectrics
Session Chairs: Jiaqing He and Bo Iversen
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 225 A

10:30 AM *EP13.01.01
Advances in the Understanding and Performance of High Performance Thermoelectrics Mercouri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

Thermoelectric solid-state energy conversion technology can provide a reliable and clean way to generate operative electricity from waste heat, which is a promising strategy for addressing energy conservation and management. Thus, there is a broad based push from the science and technology community to develop highly efficient thermoelectric materials as a possible route to address the worldwide power generation problem from heat. Today there is a variety of effective strategies to improve the properties of these narrow gap semiconductors such as achieving extremely low thermal conductivity and raising the power factors. The so-called nanostructuring and mesoscale approach has led to a new era of investigation for bulk thermoelectrics. Currently lead chalcogenides incorporating second phases hold the record in figure of merit for high temperature power generation applications. Nanostructures enable effective phonon scattering of a significant portion of the phonon spectrum while mesostructures tend to scatter phonons with long mean free paths remain. By combining all relevant length-scales in a hierarchical fashion, from atomic-scale disorder and nanoscale endotaxial precipitates to mesoscale phonon scattering a large enhancement in the thermoelectric performance of bulk materials can be achieved. Progress on device and module assembly is excellent and modules with conversion efficiency of ~11% for a delta T of 590 K have been demonstrated using nanostructured PbTe-based materials. Interestingly, nanostructuring is not necessary to obtain record high thermoelectric performance. Several systems based on PbTe and PbSe will be described that lack nanostructuring but feature complex structures and point defects, which can also achieve very low thermal conductivity. Comparisons with nanostructured materials will be made. Finally, SnSe is a new striking example of a single-phase two-dimensional material which has shed new light in thermal transport and charge transport properties both in p-type and n-type doping. The state of the art in the understanding of this system will be presented.

11:00 AM *EP13.01.02
First-Principles Simulation of Electron and Phonon Transport in Thermoelectric Materials with Alloys and Defects Jiawei Zhou, Te-Huan Liu, Qian Xu, Qichen Song, Zhiwei Ding and Gang Chen; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.
This talk will discuss our recent work to simulate electron and phonon thermoelectric properties based on the density-functional theory, in particular focusing on materials with alloys and defects. Intrinsic electron transport properties are governed by carrier scatterings by phonons, but practical materials often involve alloys or have defects, that can significantly change the transport properties. The main challenge is how we can take these into account in first principles simulations and obtain more reasonable estimation for materials' thermoelectric performance. In this talk, building upon our previous experience in understanding the electron transport in semiconductors (EPL, 109, 57006, 2015; PRL, 114, 115001, 2015; PNAS, 112, 14777, 2015; PRB, 95, 075206, 2017; Nat Comm, 9, 1721, 2018; PNAS, 115, 879, 2018), I will discuss how we can extend the simulation to include alloys and defects. First, I will use two alloy systems (ZrNiSn/ZrNiPb, and Si/Ge) to illustrate what are the general effects of alloying on electron transport in comparison to phonon transport. The latter material system also gives us the opportunity to utilize the phonon drag effect to enhance the thermoelectric performance. In the second part, I will discuss how local defects (e.g. dopants, interstitials) impacts the electron transport in half-Heuslers and Zintl compounds. The ability to quantify the defect scattering not only helps to explain the discrepancy between experiment and simulation results assuming only intrinsic scattering mechanisms, but also provides guidelines for selecting optimal dopants for thermoelectric materials. This work is partially supported by S-TEC, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award No. DE-SC0001299/DE-FG02-09ER46577), and partially by DARPA MATRIX program (Grant No. HR0011-16-2-0041).

11:30 AM EP13.01.03
High-Throughput Screening for Thermoelectric Material and Transport Descriptors D V M. Repaka,1 Ady Suvardi,1 Zekun Ren1,2, Tonio Buonassisi1,3 and Kedar Hippalgaonkar1,4 1Institute of Materials Research and Engineering, Singapore, Singapore; 2MSE, Nanyang Technological University, Singapore, Singapore; 3ME, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4National University of Singapore, Singapore, Singapore.

In the field of functional materials, there has been a lot of development in piezoelectrics, thermoelectrics and photovoltaics using Bayesian inference with a forward model to accurately determine material descriptors. So far, machine learning approaches have only been used to predict promising new thermoelectric compositions from density functional theory calculations, building upon open-source databases towards the discovery of high performance materials. Further, high-throughput materials screening approaches are still rudimentary, limited by the lack of universally defined material and thermoelectric transport descriptors. Finally, rapid and accurate materials characterization that can directly measure these descriptors are arduous (for example, method of four coefficients) or do not exist. In this work, we disclose a rapid and accurate way to determine the material and transport descriptors of thermoelectric performance by feeding simple single-leg power-load experimental data to a Bayesian machine learning algorithm using Boltzmann transport theory. Employing only two input parameters (temperature gradient and external load resistance) and the observed power output, the Bayesian inference algorithm is able to extract thermoelectric parameters ranging from material-layer properties (Seebeck coefficient, electrical resistivity) to transport-layer characteristics (energy-dependent scattering parameter, band gap offset, etc.) as well as extrinsic contributions such as parasitic contact resistance. In addition, systematic error from measurement can also be identified and corrected. Hence, we are able to predict band and transport descriptors that can be measured directly using experiments for the first time. While these reveal the complex dynamics of scattering in thermoelectric materials, we envision that they will also provide universal screening criteria for high performance thermoelectrics in the near future.

11:45 AM EP13.01.04
Integrated Micro-Thermoelectric Coolers with Free-Standing Design and Robust Device Performance Guodong Li1, Javier Garcia1, David Alberto Lara Ramos2,3, Vida Barati1,2, Nicolas Perez1, Ivan Soldatov1, Heiko Reith1, Gabi Schiering1 and Kornelius Nielsch1,2 1Leibniz Institute for Solid State and Materials Research Dresden, Dresden, Germany; 2Institute for Materials Science, Dresden University of Technology, Dresden, Germany; 3Consejo Nacional de Ciencia y Tecnologia, Ciudad de Mexico, Mexico.

Fabrication of micro-thermoelectric modules is needed in order to realize on-chip integrated power generation as a solid-state thermoelectric generator (TEG) and local heat management as a Peltier cooler (TEC). The main challenges lie in the development of a feasible and cost-effective technology, which needs to be compatible with the modern semiconductor fabrication technology. In this work, integrated micro-thermoelectric coolers (μ-TECs) based on the telluride compounds, with a packing density over 5500 leg pairs per cm² and an optimized net cooling around 6 K near room temperature, have been successfully fabricated by combining conventional techniques of photolithography and electro-chemical deposition (ECD). Systematical device characterizations, including current and temperature dependent cooling performances, transient cooling response, cycling reliability, and long-term stability under constant current, have been examined and demonstrated. Particularly, the as-fabricated μ-TECs show a reliability up to 10 million cycles and cooling stability under constant current for more than 1 month under ambient environment. Further, a transient cooling response time of 1 ms outperforms that of devices reported in the literatures by at least one order of magnitude. Model simulations based on the finite-element method (FEM) and analytical calculations both show consistency with the experimental results, indicating high quality thermoelectric materials (for both n and p legs) and negligible contact resistances in the as-fabricated μ-TECs.


1:30 PM • EP13.02.01
Tuning the Electrical Transport in Rashba Spin-Split BiTel Lihua Wu and Jihui Yang; University of Washington, Seattle, Washington, United States.

Crystal structure inversion asymmetry and strong spin-orbital coupling can induce a Rashba-type spin-split effect on the electronic band structures of materials, which has been intensively studied in diverse fields of condensed matter physics and materials science. Bulk BiTel compound possesses a giant Rashba spin-split band dispersion with a unique Fermi surface topology evolution across the Dirac point. The dimensionality reduction in the density of states can lead to beneficial thermoelectric responses in bulk and few-layer-thick BiTel, when the Fermi level is below the band-crossing point. In this talk I will present our recent data and analysis of the Shubnikov de Haas oscillations to distinguish electrons of the inner and outer Fermi surfaces. We also studied topological phase transitions and changes in the electrical transport properties by applying uniaxial strain on micro-size samples. Our data suggest that from bulk to few-layers, BiTel offers an interesting platform for exploring new degrees of control for quantum materials.

2:00 PM • EP13.02.02
Electric and Thermal Conduction Behavior of Layered-Oxide Thermoelectric Ceramics Yuhanhua Lin, Guangkun Ren, Xin Tan and Cewen Nan; School of Materials Science and Engineering, Tsinghua University, Beijing, China.

In comparison with thermoelectric alloys, oxide semiconductors, which are thermally and chemically stable in air at high temperature, are regarded as the promising candidates for high-temperature thermoelectric applications in waste-heat recovery and power generation, such as solar energy harvesting through solar concentrators. However, the ZT values of the oxide ceramics still remain rather low in comparison with their alloy counterparts due to the medium electrical conductivity and high thermal conductivity. In this talk, we focus mainly on our works on layered BiCuSeO, Bi2SeO and Cu2O-CuO ceramics. The special layered structure can effectively scatter the phonons, resulting in an obvious reduction of thermal conductivity. Further by engineering the band structure and nanostructures, the thermoelectric properties can be significantly improved, and a high performance oxyselenide BiCuSeO ceramic with ZT>1.5 at 823 K was developed.

2:30 PM • EP13.02.03
Spin Effects Leading to zT>1: MnTe(Cr) vs MnTe(Li) Md Moharab Hossain Polash1, Vladislav Perelygin2, Morteza Rasoulianboroujeni1, Yuhanhua Zheng1, Tianqi Lu1, Ning Liu3, Michael Manley4, Raphael Hermann5, Alex Smirnov2, Joseph P. Heremans6,7,8,9,10,11, Huizhou Zhao1 and Daryoosh Vashaee1,2 1Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2Department of Chemistry, North Carolina State University, Raleigh, North Carolina, United States; 3Department of Developmental Science, Marquette University, Milwaukee, Wisconsin, United States; 4Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio, United States; 5Institute of Physics, Chinese Academy of Sciences, Beijing, China; 6Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 7School of Materials Science and Engineering, Tsinghua University, Beijing, China; 8Department of Materials Science and Technology, Tsinghua University, Beijing, China; 9Renmin University of China, Beijing, China; 10Zhejiang University, Hangzhou, China; 11Department of Physics, Zhejiang University, Hangzhou, China.
Antiferromagnetic MnTe:Li has shown a benevolent strong spin effect on thermoelectric properties across a broad range of temperature leading to $ZT>1$ at 900K [1,2]. Strong spin contribution to the heat capacity and spin disorder scattering effect on carrier mobility is observed near the Neel temperature, $T_N=307K$. However, the spin contribution to the thermopower continues above $T_S$ and extends up to 900K. Spin contribution to those properties below $T_S$ has been attributed to the magnon-drag effect [3], while spin effects on thermopower above $T_S$ are associated to the paramagnon-drag originated from the mid or short-range magnetic ordering [2]. Neutron inelastic spectroscopy and specific heat data showed an agreement to that theory to some extent while some competing theories such as the spin-fluctuations and spin entropy can also explain thermopower enhancement in magnetic materials [1,4]. To investigate the validity of those theories, we synthesized MnTe with different dopants to modify the magnetic properties and study their effects on the thermoelectric characteristics. In particular, Cr-doping was introduced to the MnTe system to break the antiferromagnetic ordering intentionally. MnTe doped with 5% and 14% Cr showed ferromagnetic properties with Curie temperature of ~100K with the magnetic moments reducing monotonically at above 100K. The specific heat, however, still showed the strong contribution from the magnon heat capacity near 300K despite lack of obvious magnetic phase transition at or near that temperature. The presence of ferromagnetic ordering in MnTe:Cr observed in the magnetic measurement is attributed to the spin-polarized hole-mediated magnetic interaction, while magnons observed in specific heat measurement can be associated to the presence of remnant short-range antiferromagnetic ordering. The breaking of the antiferromagnetic ordering suppresses the magnon and paramagnon contributions to the thermopower in MnTe:Cr. Cr-doping overall exhibited detrimental effects on the thermoelectric behavior of MnTe due to the modifications in magnon hole interactions. We will discuss the results obtained on thermoelectric properties and compare them with those of Li-doped MnTe.


3:30 PM *EP13.03.01

Paramagnetic Dragan as a Route to High ZT
Joseph P. Heremans,1 Yu-Nhua Zheng,1 Tianqi Lu1, Md Mobarak Hossain Polash1, Morteza Rasoulihanboroujeni1, Ning Liu1, Michael Manley2, Yuan Deng6, Peijie Sun6, Xiaolong Chen5, Raphael Hermann3, Dariohosh Vashe3, and Huaizhou Zhao4; The Ohio State University, Columbus, Ohio, United States; 1North Carolina State University, Raleigh, North Carolina, United States; 2Marquette University, Milwaukee, Wisconsin, United States; 3Institute of Physics, Chinese Academy of Sciences, Beijing, China; 4Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 5University of the Negev, Be'er Sheva, Israel.

Thermal spin transport can be used as a new, independent variable that alleviates the counter-indicated nature of the parameters that enter ZT. Fermi-Dirac statistics impose an inverse relation between the thermopower and the carrier concentration, and thus, the electrical conductivity. However, this condition does not exist for bosons, like magnons, whose magnonic thermopower is the entropy per particle [1]. For example, magnon drag can boost the thermopower of ferromagnetic metals [2]. In this talk, we will first outline how magnon drag also increases the thermopower of the antiferromagnetic (AFM) semiconductor MnTe doped with the aliovalent acceptor Li by about a factor of 3 near the ordering temperature $T_N=307K$. Surprisingly, the boost in thermopower persists in the paramagnetic (PM) regime up to above 900 K. This enables optimally doped MnTe to reach ZT values in excess of 1 at $T>850K$. We ascribe the increase in thermopower to the drag (transfer of linear momentum) of electrons by the local thermal fluctuations of the magnetization in the paramagnetic state, paramagnons. Neutron scattering identifies the magnon density of states in the AFM regime. An excess density of states remains visible up to the maximum temperature of the measurements, 450 K. From the energy width of this line, a paramagnons lifetime of $3x10^{-14}s$, is derived. The spin-spin correlation length in the PM state is then further derived to be about 2.5 nm from this and the momentum linewidth. The energy scattering time of electrons derived from the mobility is 2-to-5 x $10^{-14}s$, about 10 times smaller than the paramagnons’ lifetime. The de Broglie wavelength and the effective Bohr radius of the electrons are both shorter than the spin-spin correlation length. Consequently, from the electron point of view, paramagnons behave like magnons in the ordered state and contribute a drag thermopower that is the main mechanism behind the high ZT. This is the first example of a spin-based effect that is much larger than a charge-based effect, and leads to a technologically significant thermoelectric performance. If this observation can be verified in other classes of paramagnetic semiconductors, of which there may be many, it could open a new direction for thermoelectrics research.

The work is supported by then ARO MURI “Materials with extraordinary spin/heat coupling, grant W911NF-14-1-0016

4:00 PM *EP13.03.02

Chiral Fermion Transport and Their Thermoelectric Properties
Qiang Li; Brookhaven National Laboratory, Upton, New York, United States.

Chiral fermions exist in the expanding class of quantum materials that display some unique transport properties, including negative longitudinal magnetoresistance via chiral magnetic effect, anomalous Hall effect, and anomalous Nernst effect that may be exploited for thermomagnetic cooling. Among the contributing factors to these unique properties are linear electronic band dispersion, chirality, and Berry curvature in chiral fermion systems. Interesting, many chiral materials were discovered in the compounds that are normally investigated for their superior thermoelectric performance. In this presentation, we will present our studies attempting to capture the fundamental difference in seemingly similar behavior in the transport properties of chiral materials and trivial thermoelectric materials. I will also discuss how to experimentally identify which mechanism is the result of chiral fermions.

4:30 PM EP13.03.03

First-Principles Defect Calculations to Dopability Predictions in Thermoelectric Materials
Anuj Goyal, Prashun Gorai and Vladan Stevanovic; Colorado School of Mines, Golden, Colorado, United States.
Dopability is important for thermoelectrics as it represents the ability to control carrier concentration of a semiconductor material. However, general understanding of factors governing dopability is largely missing which makes dopability predictions very difficult. To address this problem we aim to develop a predictive model that allows rapid computational assessment of the dopability of materials. As a first step, we have build a training set of accurate point defect calculations obtained using our robust ab initio computational framework to calculate point defect energetics using modern defect theory. Automation tool has thus enabled us to build a large dataset of first-principles defect calculations on a diverse set of thermoelectric-relevant materials. As a second step, we use this training set to develop dopability prediction model that can effectively correlate set of easily accessible bulk-derived properties to defect formation energies and carrier concentrations. Our analysis focuses on structural as well as compositional properties, bulk formation enthalpy, chemical potentials, and details of the electronic structure such as band dispersion, band gap, absolute band edge position, etc. Ultimately, this procedure allows us to parameterize dominant bulk properties that will be important in achieving reliable dopability predictions.

SESSION EP13.04: Layered Structures
Session Chairs: Theodora Kyratsi and G. Snyder
Wednesday Morning, April 24, 2019
PCC North, 200 Level, Room 225 A

8:00 AM *EP13.04.01
Engineering Thermal and Electrical Interfaces and Grain Boundaries in Thermoelectric Materials G. J. Snyder; Northwestern University, Evanston, Illinois, United States.

To devise strategies for improving the thermoelectric performance of materials, it is essential to understand the coupled charge and thermal transport mechanisms. In heavily doped semiconductors for example we often expect ionized impurity scattering to dominate electrical transport especially when mobility increasing with temperature is observed. However, the inadequacy of this description in thermoelectric materials such as the new high-performance n-type MgSb2, becomes apparent when trying to consistently explain various experimental observations like the enhanced mobilities in larger grain samples and sharp crossovers to metal-like mobilities that decrease with temperature. The underlying cause of such complications is largely associated with the conventional Mathiessen’s rule that interprets or models all of the charge carrier scattering as homogeneous events. The inhomogeneous nature of materials, such as that caused by grain boundaries, must be taken into account to rethink engineering strategies and further improve thermoelectric materials. Prevailing models for thermal transport treat interfaces and grain boundaries as structureless even though at the atomic scale they are better described as arrays of linear defects of various types. Allowing for this inherent structure, several fundamental characteristics of heat transport arise, such as diffraction conditions when heat carrying phonons scatter off the periodic, linear defect arrays that should be present in grain boundaries. Furthermore, a dimensionality crossover is observed in diffusive heat transport where phonons with a wavelength longer than the linear defect spacing see the interface simply as a structureless planar defect, and phonons with see with the interface as a collection of independently scattering linear defects.


8:30 AM *EP13.04.02
Layered Thermoelectric Materials Bo B. Iversen, Department of Chemistry, Aarhus University, Aarhus, Denmark.

Layered (2D) materials exhibit a variety of extraordinary properties, and recent focus has included topological insulators, electrode materials, monolayers, hetero structures – and thermoelectrics. The physical properties such as band gap or thermal and electrical conductivity are related to the detailed structural characteristics as well as the specific chemical bonding both within the covalent layers and across the van der Waal gap. It is generally assumed that layered materials exhibit anisotropic properties, but the properties are rarely discussed in direct relation to the specific chemical bonding characteristics of the solid. Using advanced crystallographic analysis including charge density modelling as well as ab initio theoretical calculations, we have studied the crystal structures and chemical bonding of a range of important layered thermoelectric materials including Cu2Se [1], MgSb2 [2], SnS2 [3], TiS2 [4] and SnSe [5]


9:00 AM EP13.04.03
Improved Stability and High Thermoelectric Performance Through Cation Site Doping in N-Type La-Doped MgSb2,Bi4S2 Max Wood, Kazuki Imasato, Jimmy J. Kuo and G. J. Snyder; Northwestern University, Chicago, Illinois, United States.

Until Recently only chalcogen (S, Se, Te) anion site dopants had been considered tested for n-type MgSb2 type materials. Herein is showed how n-Type conduction in a MgSb2, Bi4S2 system is achieved with La-doping at cation sites with a peak $zT > 1$. La-doped samples exhibit much higher doping efficiency and dopability compared to other chalcogen-doped samples, which allows for greater tunability of the electronic properties. La-doping also significantly improves the thermal stability of n-type MgSb2, Bi4S2 measured via a long-term Seebeck and Hall carrier concentration measurements. This increased stability in La doped material suggests new pathways to engineer around the degradation of electronic properties witnessed in this and other thermoelectric materials.

The Effect of Mn Doping and Porosity on the Transport Properties of Thermoelectric Alloys in the MgSb2 Family Yuanhua Zheng1, Siyi Chang2, Joseph P. Heremans1 and Haizhou Zhou1, 1The Ohio State University, Columbus, Ohio, United States; 2Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Considering the cost of tellurium, it is technologically important to find alternatives to the well-known Bi2Te3-based tetradymite family of thermoelectric materials for cooling applications near room temperature, and power generation applications below 300 °C. The MgSb2 family of materials is a promising candidate [1], specifically MgS1-xMnxSb2. We investigate here the effect of Mn doping of this material by the method of the four coefficients [2]. In this method, the four transport coefficients, resistivity, and Hall, Seebeck and Nernst effects are measured, and used to calculate the charge carrier concentration, mobility, density of states effective mass $m^*$, and scattering exponent $\lambda$ (defined by the energy (E) dependence of the relaxation time, $\tau(E) \propto E^{\lambda-\alpha}$). We then further study the effects of making the samples porous. Thus resonance or Kondo effects are separated from the effects of changes in scattering mechanisms.


9:30 AM EP13.04.05
Nano-Structuring of Bi2Te3-Se: Toward High Thermoelectric Performance Sang-Soon Lim1, Kwang-Chon Kim1, Hyung-Go Park2, Seung-Hyub Baek1, Seong Keun Kim1 and Jin-Sang Kim1, 1Center for Electronic Materials, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Department of Materials Science and Engineering, Yonsei University, Seoul, Korea (the Republic of).
Thermoelectric materials should have a high electrical conductivity and a low thermal conductivity simultaneously to realize high thermoelectric figure-of-merit ($ZT$). However, the intimate coupling between electrical conductivity and thermal conductivity renders the enhancement of thermoelectric performance difficult. Nano-structuring of thermoelectric materials has been a major strategy to improve the thermoelectric performance because the phonon scattering at nano-grain boundaries effectively reduces the thermal conductivity without significant loss of electronic carrier.

Here, we propose a novel strategy with atomic layer deposition (ALD) for nano-structuring of Bi$_2$Te$_3$-Se, thermoelectric element to achieve a low thermal conductivity. The ALD technique is known to allow a precise thickness control at a sub-nm scale and have excellent conformality even on complex shaped substrate. Conformal ZnO layers were grown on the very fine Bi$_2$Te$_3$-Se powders. The Bi$_2$Te$_3$-Se/ZnO core-shell structured powders were sintered by a spark plasma sintering process and a hot-extrusion process. The ZnO-coated Bi$_2$Te$_3$-Se thermoelectric element shows small grains compared to the uncoated Bi$_2$Te$_3$-Se$_x$. The thermal conductivity is significantly decreased by the small grains and the thin ZnO layer at the grain boundaries. Consequently, the figure-of-merit of the n-type Bi$_2$Te$_3$-Se$_x$ is improved. Furthermore, the mechanical strength of the materials is enhanced by the ZnO ALD coating. Therefore, we believe that the nano-structuring of the Bi$_2$Te$_3$-Se$_x$ with ALD contributes to enhance thermoelectric performance of Bi$_2$Te$_3$-related materials.

9:45 AM EP13.04.06
Rapid Solid-State Reaction and Simultaneous Sintering of Nanostructured Thermoelectric Materials Using Microwave Radiation
Abhishek Malhotra$^1$ and Daryoosh Vashaee$^{1,2}$
$^1$Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina, United States; $^2$Material Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Nanostructuring in some materials can reduce the thermal conductivity more than cutting the thermoelectric power factor leading to $ZT$ improvement. With the quest to make and test the nanostructured forms of a variety of the known good thermoelectric materials, efficient material synthesis methods become highly desired. The conventional method of synthesis is based on a multi-step process involving ball milling, melt-quenching, and sintering, which requires a significant amount of time and energy. We introduce an alternatively faster approach based on electromagnetic field induced reaction and sintering using microwave (MW) radiation that can produce nanostructured bulk compounds with excellent properties compared to the conventional methods. This is a two-step process involving the uniform mixing of the elements and followed by MW radiation. The synthesis happens at a temperature lower than the melting point with the energy heating only the material (and not the entire furnace), which lowers the overall power requirement. MW radiation has been shown to enhance diffusion rates[i] and results in an accelerated solid-state reaction. Compared to other rapid alloying methods, such as self-propagating high-temperature synthesis, there is no limit to the type of compounds that can be synthesized. Furthermore, the consolidation happens simultaneously during the reaction and does not require additional densification steps.

Achieving crystallite sizes less than 20 nm is often difficult in bulk structures using conventional sintering methods such as hot pressing and spark plasma sintering. The main obstacle is that during the sintering, the grains grow, and nanoscale features broaden or diminish. Reducing the sintering time does not help either, as the material would not be adequately sintered resulting in low carrier mobility. Therefore, the sintered materials often have average crystallites larger than 20-30 nm in size at best. Interestingly, MW radiation has also shown decrystallization effects which further reduces the requirement of other nanostructuring steps. MW synthesis can generate structures with sub-10nm crystallites appropriate to achieve high ZTs in some materials.[ii]

This study has focused on the synthesis of nanostructured Bi-Sb-Te-Se alloys. The elemental powders were mixed in the required stoichiometry and sintered under MW radiation. No other source of heating was used. Materials used for this study were Bi-Sb-Te, Bi-Te and Sb-Te alloys, which are known for their thermoelectric properties near room temperature. The elemental powders were mixed for 15 minutes, cold-pressed, loaded into a die, and sintered in a MW cavity. Samples were consolidated at different temperatures ranging from 325 °C to 425 °C in steps of 25 °C. The x-ray diffraction (XRD) analysis of the mixed powder before MW sintering showed diffraction lines of the elemental materials with no sign of solid-state reaction after the short mixing time. However, the XRD analysis of the microwave processed samples showed a complete solid-state reaction with no trace of the elements. It was observed that the alloy entirely formed at 325 °C. Differential Scanning Calorimetry analysis was performed on these samples which further confirmed the formation of the alloy after the MW sintering. We will discuss the processing steps of MW sintering, material characteristics, and the thermoelectric properties of the synthesized materials.


10:00 AM BREAK

10:30 AM EP13.05.01
Revealing Heat Transport and Phonon Scattering Using Electron Probes—Challenges and Opportunities
Yimei Zhu; Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York, United States.

Modern electron microscopy, especially combined with the aberration correction and monochrometization technologies, has changed the way we visualize materials across a wide range of length scales. Nevertheless, revealing thermal transport and phonon scattering mechanisms in materials with electrons still poses a major challenge. In this talk, I will first describe the electron microscopy method we developed to understand the role of lattice disorder on phonon scattering by accurately measuring local static displacement and thermal vibration via simultaneous acquisition of multiple annular-dark-field images at different electron-scattering-angles. Layered caborlates, which exhibits unusually large thermoelectric power, will be used as an example. The system consists of a soft-rigid layered crystal structure with incommensurate displacive-modulation and local atomic vibrations. Through structure determination and refinement using electron microscopy and quantum field theory we show the specific combination of highly crystalline and strongly distorted layers is essential for enabling large electronic-conductivity and low thermoconductivity that is associated with efficient phonon scattering. We further demonstrate besides the well-known Umklapp, Rayleigh and displacement phonon scattering mechanisms, additional resonance and anharmonic scattering play an extremely important role in layered materials. As for future opportunities, I will give an overview on the RF-gun-based 2.8MeV ultrafast electron microscope we recently developed at BNL that has achieved 120fs resolution with 10$^6$ electrons per pulse. Brief examples will be given on how we probe the time-resolved interactions between charge, orbital and lattice and separate the roles of various phonon modes as well as thermal transport in function materials using ultrafast pump-probe approach.

The author would like to thank the members of the Electron Microscopy and Nannstrucure Group at BNL, the work at BNL is supported by US DOE, Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-SC0012704.

11:00 AM EP13.05.02
Thermoelectric Properties and Topology of Phosphides
Claudia Felsen$^1$, Johannes Gooth$^2$, Satya N. Guin$^2$, Chenguang Fu$^2$ and Sarah J. Watzman$^1$
$^1$Department of Mechanical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio, United States; $^2$Solid State Chemistry, Max Planck Institute Chemical Physics of Solids, Dresden, Germany.

Topology, a mathematical concept, became recently a hot topic in condensed matter physics and materials science. The topology of the electronic structure of a material determines the electronic, thermal and magnetic properties of solids. All known materials can be reclassified through the lens of topology [1]. Beside of Weyl and Dirac fermions, new
fermions can be identified via linear and quadratic 3-, 6- and 8-band crossings stabilized by space group symmetries [2]. Weyl semimetals, a new class of topological phases were found in NbP, NbAs, TaP, MoP and WP [3-13]. In NbP nano wires we have observed the chiral and a mixed gravitational anomaly [9, 10]. Additionally, NbP [10] and WP [11] show evidence for a hydrodynamic flow of electrons, which violated strongly the Wiemann-Franz law. MoP and WP show exceptional transport properties such as high conductivity (better than copper), high mobilities and a large magneto-resistance [6, 7]. In WP2 a transition from a hydrodynamic electron fluid below 15 K into a conventional metallic state at higher temperatures is observed in thermal and magneto-electric transport experiments [11]. The hydrodynamic regime is characterized by a viscosity-induced dependence of the electrical resistivity on the square of the channel width that coincides with as strong violation of the Wiedemann-Franz law. Single crystalline NbP shows an exceptional high Nernst-effect with a strong magnetic field dependence [12, 13]. Even polycrystalline, spark plasma sintered samples of NbP show still a large Nernst thermopower value of ~90 μV/K and power factor of ~35×10−4 W mK−2 at 9 Tesla. Also in magnetic samples, such as Co2MnAl and Co2MnSe2, we can design giant Nernst effects due to an strongly enhanced Berry curvature [14, 15]. In general, the concept of topology might enable us to design more energy efficient materials for thermoelectric applications and beyond.


11:30 AM EP13.05.03
Slow Diffusion-Fast Vibration Model in Superionic Conductor Thermoelectric AgCrSe2
Lin Xie, Di Wu, Hongliang Yang, Yong Yu, Yifan Wang and Jiaping He;
Department of Physics, Southern University of Science and Technology, Shenzhen, China.

Phonon Liquid-Electron Crystal (PLEC) thermoelectric materials based on superionic conductors have attracted a number of research interest for their ultralow lattice thermal conductivity. It is proposed that the mobile ions are liquid-like, which either gives rise to a reduction of specific heat from the solid limit to the liquid limit, or the vanish of mean potential for transverse waves. However, it is debated if the timescale of the mobile ions is fast enough to interrupt phonon and the low is instead attributed to anharmonicity. In this talk, we will report the study of superionic conductor AgCrSe2, from the low temperature metallic phase to the high temperature superionic phase by in-situ scanning transmission electron microscopy (STEM) and ab-initio molecular dynamics simulation. We discovered that the mobile Ag+ ions in the “liquid-like” superionic phase are not randomly distributed in between neighboring CrSe2 layers as in liquids, but on average still tend to dwell at lattice sites as in a positional disorder solid. The preferential occupation of mobile ions at lattice sites indicates that the diffusing ions are weakly bonded to a potential and thus they cannot move freely as in liquids. According to our theoretical calculations, it is revealed that the characteristic timescale for Ag+ diffusion is relatively slower than phonon vibrations. The calculated probability distribution of Ag+ atoms also demonstrates the same preferential occupation at lattice sites feature as observed experimentally. Therefore, the ion diffusion and vibrations are decoupled in a slow diffusion-fast vibrations way and we suggest that diffusion is not able to strongly interrupt phonon vibrations. Instead, phonon vibrations are significantly affected by the cation disorder, just as in phonon glass thermoelectric materials. The ultralow of AgCrSe2 at its superionic phase can be explained by disorder according to the lattice gas model or Cahill’s model for disordered solids.

11:45 AM EP13.05.04
Thermoelectric Transport Properties of Iodine Doped Phthalocyanine Copper (CuPc)
Yanling Chen and Lidong Chen; Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, China.

Metal phthalocyanine compounds are considered as the potential thermoelectric materials because of their good heat and chemical stability. But the poor electrical transport properties greatly impede their application. Chemical doping is an efficient method to optimize the electrical transport properties of organic semiconductors. In this work, we systematically studied the effect of iodine doping on the thermoelectric properties of copper phthalocyanine (CuPc). A series of CuPcI (x=0, 0.5, 0.75, 1.0, 1.25, 1.5, 1.6 and 1.75) were prepared by heating in an iodine ambient at 400 K. The microstructure and charge carrier transport process of the CuPcI were characterized by XRD, SEM, XPS, c-AFM and PPMS. The results suggested that CuPc could be successully doped by iodine and formed two phases CuPc and CuPcI. The amount of the two phases could be detected by the XRD refinement and ion chromatography. The electrical conductivity of iodine doped CuPc samples significantly increased in comparison to the pristine sample, which was due to formation of the three dimension percolation path of the conductive CuPcI. Moreover, it was noticed that the electrical conductivity and Seebeck coefficient of these iodine samples were decoupled, which was ascribed to the low electron energy filtration effect introduced by the CuPc/CuPcI interface. As a result, the highest electrical conductivity of iodine doped CuPc was up to 914 Sm−1, about 11 orders of magnitude of the undoped sample, and the maximum seebeck coefficient of 65 μV K−1 was obtained. Finally the optimum ZT value reached 0.038 at 300 K.
of each atom using Zintl chemistry that offsets the energy penalty of forming defects in nearly all cases. Thus, we propose a valence balanced rule to understand the ground state stability of half-Heuslers irrespective of stoichiometry and nominal electron count (8, 18 or 19). Using this generalized rule we (a) predict 16 previously unreported nominal 19-electron XYZ half-Heuslers, (b) rationalize the reports of giant off-stoichiometries in compounds such as Ti₇₅₅NiSb which has been known for over 50 years and (c) discover a new class of low thermal conductivity quaternary half-Heuslers. Of the new compounds predicted here, new ternary (Ti₅₁₅PbSb) and quaternary compounds were synthesized and the half-Heusler phase confirmed through X-ray studies. Thermoelectric performance of typical defect-free half-Heuslers based on equiatomic XYZ stoichiometry are limited by their intrinsically high thermal conductivity. Flexibility in stoichiometric control of the half-Heusler systems to attain a stable valence balanced composition by accommodating large defect concentrations opens up new dimensions of low thermal conductivity defective half-Heuslers.

2:15 PM EP13.06.03

The high demand on cost-effective renewable power generation has led to intensified research interest in thermoelectric (TE) materials. Filled skutterudite alloys have attracted the greatest interest due to their suitable band gap, high carrier mobility, low-cost and benign constituent elements. In order to further lower the thermal conductivity and improve figure of merit, multi-fillers, e.g. Yb, Eu, La, Ba, Na etc., have been considered to maximize the phonon resonant scattering resulting from varying vibrational frequencies of fillers. However, the correlated behavior of electrical conductivity, Seebeck coefficient and thermal conductivity has limited the gain in figure of merit (ZT). Bulk heterojunction structure in organic solar cells offers a good mechanism for optimized electron transport. In the present study, mixed alloy comprising of (Ba, Yb, Ca₃,Co₃Sb₄, and In₃,Co₃Sb₂, was obtained by high energy ball milling and characterized for TE performance. High ZT values of 1.3 at 700 K have been achieved. The mixture of two different compounds induces an isotype heterojunction structure, which results in enhanced carrier mobility. A DFT calculation on the mixed materials band structure is conducted to understand the formation of heterojunction. Nano-grains achieved by high energy ball milling enhances the phonon scattering on mesoscale level and decreases thermal conductivity due to the decrease of thermal diffusivity and heat capacity. Quantum effect on electron transport based on both theoretical calculation and Hall measurement have been discussed.

2:30 PM BREAK

Wednesday Afternoon, April 24, 2019
PCC North, 200 Level, Room 225 A

3:30 PM *EP13.07.01
Intrinsically Low Thermal Conductivity in Metal Chalcogenides for High Performance Thermoelectric Energy Conversion Kanishka Biswas; New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India.

One of the fundamental challenges in developing high-performance thermoelectric materials has been to achieve low lattice thermal conductivity (κ_L). The exploration of new materials with intrinsically low κ_L along with a microscopic understanding of the underlying correlations among bonding, lattice dynamics and phonon transport is fundamentally important towards designing promising thermoelectric materials. InTe [i.e. In²⁺Te⁻], a mixed valent compound, exhibit an ultralow κ_L, which manifests an intrinsic bonding asymmetry with coexistent cationic and anionic substructures. The phonon dispersion of InTe exhibits, in addition to low-energy flat branches, weak instabilities associated with the rattling vibrations of In⁺ atoms along the columnar ionic substructure. These weakly unstable phonons originate from the 5s lone pairs of adjacent In⁺ atoms and are strongly anharmonic, which scatter the heat-carrying acoustic phonons through phonon-phonon interactions. Similarly, a Zintl compound, TlInTe, also exhibit ultralow κ_L due to low energy rattling modes of weakly bound Tl⁺. Soft phonon modes and optical-acoustic phonon coupling cause an ultralow lattice thermal conductivity in the room-temperature hexagonal phase of AgCuTe, while the dynamic disorder of Ag/Cu cations leads to reduced phonon frequencies and mean free paths in the high-temperature rocksalt phase. A high thermoelectric figure of merit (ZT) of 1.6 is achieved in the p-type AgCuTe at ~670 K. Recently, we have shown that the localized vibrations of Bi bilayer leading to ultralow lattice thermal conductivity and high thermoelectric performance in weak topological insulator n-type BiSe near room temperature.


4:00 PM EP13.07.02
N-Type Cubic GeSe Stabilized by Entropy Driven Alloying of AgBiSe₃ Leads to Ultralow Thermal Conductivity and Promising Thermoelectric Performance Subhajit Roychowdhury, Tanmoy Ghosh, Raaga Arora, Umesh V Waghmare and Kanishka Biswas; JNCASR, Bangalore, India.

n-type Ge-chalcogenides with promising thermoelectric performance is urgently needed to match their p-type counterparts. However, their realization remains elusive due to intrinsic Ge vacancies which make them p-type semiconductors. GeSe crystallizes into a layered orthorhombic structure similar to the SnSe at ambient conditions. High symmetry cubic phase of GeSe is predicted to be stabilized either by applying external pressure of 7 GPa or by enhancing the entropy through solid solution mixing. The interplay of positive and negative chemical pressure anomalously changes the band gap of GeSe with increasing the AgBiSe₃ concentration. The band gap of n-type cubic (GeSe)ₙ(1-x)(AgBiSe₃)ₓ possesses a value in the 0.3-0.4 eV range, which is significantly lower than orthorhombic GeSe (1.1 eV). Cubic (GeSe)ₙ(1-x)(AgBiSe₃)ₓ exhibits an ultralow lattice thermal conductivity (κ_L ~ 0.43 Wm⁻¹K⁻¹) in the 300-723 K temperature range. The low κ_L is attributed to significant phonon scattering by entropy driven enhanced solid solution point defects.


4:15 PM EP13.07.03
Study of Thermoelectric Properties of Mixed Phase Bi₂Se₃ Films Made by Electrodeposition Md Golam Rosul, 1 Rasim Ahmed,2 Mona Zebarjadi,1, 2 and Giovanni Zangari; 1Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia, United States; 2Materials Science and Engineering, University of Virginia, Charlottesville, Virginia, United States.

Polymorphism in Bi₂Se₃ allows it to be tuned for unique electrical, thermal and optical properties. The commonly reported rhombohedral structure exhibits semi-metallic properties corresponding to a band gap of 0.32 eV and has been widely studied for thermoelectric applications and as topological insulators. The alternative orthorhombic structure is more semiconducting and has been reported to have a band gap close to 1.2 eV. The opportunity to fabricate a mixture of these orthorhombic and rhombohedral structures provides a chance for materials engineering with the aim of optimizing its electrical and thermal properties. Here we report the room temperature Seebeck coefficient and electrical resistance of mixed phase n-type Bi₂Se₃ films. Bi₂Se₃ films with Bi:Se atomic fraction of 38:62 was prepared by electrodeposition using an acidic bath. The XRD pattern of the electrodeposited Bi₂Se₃ films confirmed the existence of a mixed phase structure where the orthorhombic phase was found to be improved upon emergence and subsequent
Thermoelectric materials enable direct conversion between electricity and thermal energy. Therefore, most of previous studies on thermoelectric materials focus on the electrical and thermal properties. Herein we will explore the interesting optical properties of thermoelectric materials. First, we demonstrate the promising ultra-broadband phonon-enhanced optical properties. Precise control of carrier density is essential to synthesize high-performance thermoelectric materials. Doping by impurities is often frustrated in n-type Bi2Te3 alloys by incomplete activation, bipolar doping, the formation of secondary phases, and prevailing intrinsic point defects such as vacancies. This weakens the reproducibility of synthesis processes and reduces the long-term reliability of material performance. Hence, aging. Here, we explore an impurity-free doping technique to synthesize n-type bismuth tellurium selenides, combining a cold deformation and a hot extrusion. The cold deformation enables controlling the electron density in the range of \( \sim 10^{19} \text{ cm}^{-3} \). Consequently, the development of innovative technology for energy conservation in the cement industry is urgently needed. The large amount of energy from exhaust gases could potentially be used for waste heat energy recovery to generate other forms of energy. Thermoelectric power generators (TEG) could be used for such recovering of waste heat. In this work, the performance assessment of an exhaust thermoelectric generator for cement sector application is investigated with emphasis on the heat exchanger and the optimization of its geometric characteristics. A pin-fin array was considered into the exhaust duct to form the heat absorber, which could increase the heat-exchange surface area and time. This is expected to increase the temperature on the hot side of the thermoelectric module, leading to higher energy conversion and efficiency of the device. Moreover, the influence on the efficiency of the height, length and spacing of the fins is analysed for the fixed width and length of the TEG. The influence of geometric parameters of the fins on the TEG efficiency was carried out using a standard orthogonal array of the Taguchi method. An L27 orthogonal array with four controlling factors at three levels was employed in this design of experiments method. The proposed design, through the Taguchi method, leads to a significant increase of output power and increased energy recovery of the thermoelectric generator.

Theoretical Analysis of Evaporative Cooling to Enhance the Performance of Thermoelectric Device

Due to the increasing environmental awareness and rising cost of energy, there is a growing demand to develop renewable energy systems that reduce our reliance on fossil fuels [1]. Thermoelectric generator is a promising technology that cleanly converts temperature difference to electricity on the basis of Seebeck effect. Therefore, to maximize power-generation efficiency of thermoelectric generator, except the figure of merit, ZT, should be as high as possible, the temperature differential between the hot and cold sides also should be as large as possible [2]. In this work, we utilize evaporative cooling technology as opposed to the traditional heat sink to cooling the thermoelectric generator cold side. By combining thermodynamics and heat & mass transfer theory, the numerical model of thermoelectric generator with film water evaporative cooling is established in this study. And the numerical model has been constructed to consider temperature-dependent thermoelectric material properties, heat loss due to radiation and conduction, and Thomson effect. Based on the numerical model, the performances of a typical thermoelectric generator are simulated. Here, the thermoelectric generator hot side temperature is fixed into 50-150 Celsius degree, the thermoelectric generator cold side is covered by thin film water. The ambient temperature is 25 Celsius degree, the relative humidity of the air is set from 25 to 75%. The results show that when fixed the relative humidity, the higher hot side temperature, the higher output power and efficiency; when fixed the hot side temperature, the lower relative humidity, the higher output power and efficiency. Therefore, the maximum power output of 0.272 W and the maximum efficiency of 2.25% are available when the temperature of the hot side is 150 Celsius degree and the relative humidity is 25%. The theoretical model and calculation method may be applied to the prediction and
conducting polymers (CPs) have attracted extensive attention due to the advantages of mechanical flexibility, abundant elements, nontoxicity, as well as intrinsically low thermal conductivity (k) and high electrical conductivity (σ). Among them, Poly(3,4-ethylenedioxythiophene)poly-(styrenesulfonate) (PEDOT:PSS) is a promising candidate as the next-generation thermoelectric (TE) material arising from the advantages of excellent thermal stability, high transparency, and solution preparation. In this work, the TE properties of PEDOT:PSS films were effectively improved by a sequential treatment with a binary secondary doping and solution of hydrazine in DMSO at the optimized the oxidation level. Initially, doping with formic acid and then further treated with formamide improved the σ from 0.3 to ~2604 S/cm while the Seebeck coefficient (S) decreases from 17.5 to 14.5 μV/K resulting a power factor (PF) of 54.8 μW/Km at the optimum concentration of the dopants. Then, the formic acid-formamide doped PEDOT:PSS films were further doped with a solution of DMSO and hydrazine with different hydrazine concentrations. During the DMSO-hydrazine solution doping, the σ of the films decreased from 2604 to 661.3 S/m whereas the S increased from 14.5 to 41.3 μV/K due to a decrease in the carrier concentration (n), resulting in a PF of 112.8 μW/Km at the optimum oxidation level. The obtained maximum PF is almost 11280 times higher than that shown by untreated PEDOT:PSS films. Besides the k of the pristine PEDOT:PSS films decreased from 0.59 to 0.29 W/Km due to the removal of PSS after treatment. At this lowest k value, a ZT value of ~0.12 was obtained at 300K.

There is a recent interest in semiconducting superlattice films because their low dimensionality can increase the thermal power and phonon scattering at the interface in superlattice films. However, experimental studies in all cross-plane TE properties, including thermal conductivity, Seebeck coefficient, and electrical conductivity, has not been performed from these semiconducting superlattice films, because of substantial difficulties in the direct measurement of the Seebeck coefficient and electrical conductivity. Unlike the conventional measurement method, we present technique a structure of sandwiched superlattice films between two embedded heaters as heating source, and electrodes with two Cu plates, which directly enables the investigation of the Seebeck coefficient and electrical conductivity across the AO/ZnO superlattice films, prepared by atomic layer deposition (ALD) method. Used in combination with the promising cross-plane four-point-probe 3-α method, our measurements and analysis demonstrate all cross-plane TE properties of AO/ZnO superlattice films in the temperature range from 80 to 500 K. Our experimental methodology and the obtaining results represent a significant advancement in the understating of phonon and electrical transports in nanostructured materials, especially in semiconducting superlattice films in various temperature ranges.

Metal dichalcogenide thin films, such as bismuth telluride and molybdenum disulfide were successfully deposited on different substrates using radio-frequency magnetron sputtering technique. The structural, morphological, and thermoelectric transport properties of bismuth telluride and molybdenum disulfide thin films have been investigated systematically to develop a high-efficient thermal energy harvesting thermoelectric device. The magnitude of the Seebeck coefficient of bismuth telluride thin films decreases with increase in film thickness. Bismuth telluride grown at 350°C displays a maximum Seebeck coefficient of -126 μV/K at 435 K. The performance of the device shows a very strong dependence on the different growth temperature of the film. The power factor increases from 0.009 W/mK² at Room temperature to 0.014 W/mK² at 350°C. Molybdenum disulfide films show the positive Seebeck coefficient values and their Seebeck coefficient increases with film thickness. The AFM images of bismuth telluride thin films display a root-mean-square (rms) roughness of 32.3 nanometer and molybdenum disulfide thin films show an rms roughness of 6.99 nanometer when both films were deposited at 350°C. The open-circuit voltage of 130 mV shown by the pn-junction thermoelectric generator (TEG) device at 393 K. We have demonstrated a highly efficient pn-junction TEG device for waste heat recovery applications.

The thermoelectric dream is one in which thermoelectric materials can be used for energy generation and harvesting in a commercial sense at high efficiency and low cost. Efficiency is hard to achieve for most thermoelectric as electrical and thermal conductivity are closely related and correlated. The efficiency of any thermoelectric device is given by a quantity which called the figure of merit ZT. For thermoelectric devices to be viable alternative energy source they should achieve a ZT greater than 2. Here we report on a thermoelectric device based on Bi₂Te₃/W₃S superlattice structure created through radio frequency (RF) magnetron sputtering deposition. Quantum confinement in these low dimensional layers creates a high density of carriers near the Fermi level thereby enhancing the electrical conductivity and ZT. The ZT is increased by increasing these layers through the scattering of short wavelength phonons by picking layer thicknesses less than the phonon free mean path. This makes the structure a good electrical conductor while limiting the thermal conductivity thus beginning to decouple these two material properties.

A System for Thermomagnetic Transport Properties Measurement from 80 K to 400 K Roger Dorris, Randy Sterbentz, Juan P. Tolento, Dominic Gallelli and Matt Beekman; California Polytechnic State University, San Luis Obispo, California, United States.

Experimental determination of material quantities such as the charge carrier density of states effective mass and dominant charge carrier scattering mechanism can provide important insight into the performance of thermoelectric materials, and plays a central role in contemporary thermoelectric materials research. In this context, measurement of the Nernst coefficient, which is sensitive to the scattering mechanism, provides useful additional information that complements the traditional measurement of electrical resistivity, Seebeck coefficient, and Hall coefficient. Here we describe a custom measurement system capable of measuring all four of these galvanomagnetic and thermomagnetic transport coefficients as a function of temperature from 80 K to 400 K, in magnetic fields from ~1 T to 1 T, on both bulk and thin films samples. In addition to data on the system’s
Synthesis and Thermoelectric Performance of Ceramic Composites Julius F. Rodriguez, Adam Sebastian Gutierrez and Luis Carlos Moreno; Univ Nacional de Colombia, Bogota DC, Colombia.

\[ \text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3 \] polycrystalline thermoelectric ceramics with small amounts of metallic \( \text{La}_1 \text{Sr}_2\text{CuO}_4 \) have been fabricated by solid-state reaction method. The effects of introducing metallic ceramics on the thermoelectric and transport properties of \( \text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3 \) have been studied. The transport properties were studied in the temperature range between 85 and 300K. The thermoelectric performance of \( \text{LaCoO}_3 \) ceramics was improved as a consequence of the Ca doping and metallic \( \text{La}_1 \text{Sr}_2\text{CuO}_4 \) adding. The composite exhibits maximum values for the thermoelectric power factor, PF, and the dimensionless figure of merit, ZT close to 28 mW/K²·cm and 0.5, respectively. Thus, the observed behavior in the transport properties become these composites promising materials for use in thermoelectric devices for low-temperature applications.

Relationship Between Thermoelectric Properties and Morphology of Doped P3HT Thin Films for Potential Thermoelectric Applications Jonathan J. Montes and Harold O. Lee; Norfolk State University, Norfolk, Virginia, United States.

Polymeric conjugated materials are very promising for developing future soft material-based semiconductors, conductors, electronic and optoelectronic devices due to their inherent advantages such as lightweight, flexible shape, low-cost, ease of processability, ease of scalability, etc. There are numerous ways to tune material properties via post-processing treatments. One way to enhance device performance is through the process of thermal annealing. Annealing allows for polymer thin films to self-assemble into a lower energy conformation which typically leads to better morphology and higher charge mobility. What is yet to be fully understood is how film morphology is related to the Seebeck coefficient of a material. In this study, we observed the relationship between the Seebeck coefficient, various annealing times and temperatures, and doping concentration with doped P3HT thin films. Our results can provide insight into how can develop high performance organic thermoelectric materials post-processing techniques.

Ultralow Thermal Conductivity and High Thermoelectric Figure of Merit in Polycrystalline SnSe Yong Kye Lee1,2 and In Chung3,4; Chemical and Biological Engineering, Seoul National University, Seoul, Korea (the Republic of); 3Center for Nanoparticle Research, Institute for Basic Science, Seoul, Korea (the Republic of).

A remarkably high thermoelectric figure of merit \( ZT \) of ~2.6 at 923 K was recently reported in p-type SnSe single crystals along the crystallographic b-axis. Afterward, realizing comparable thermoelectric performance in the polycrystalline counterparts have been intensively investigated. However, polycrystalline SnSe-based materials unexpectedly exhibit much higher thermal conductivity than the single crystals, resulting in far poorer thermoelectric performance in the former. In this presentation, we hypothesize that surface oxidation would be the main origin of their high thermal conductivity. To solve this issue, we introduce an oxygen-removal process under mildly reductive atmosphere. As a result, we are able to achieve the ultralow lattice thermal conductivity and thereby markedly enhanced \( ZT \) in polycrystalline SnSe-based materials, which are comparable to those in their single crystals.

Rapid Synthesis and Fabrication of Thermoelectric Materials Using Advanced Manufacturing Technique Jianxu Shi, Hualing Chen and Wnajian Wang; 1Louisiana State University, Baton Rouge, Louisiana, United States; 2Mechanical Engineering, Xian Jiaotong University, Xian, China.

The conventional forming processes for thermoelectric bulk materials, such as hot press, cold press, spark plasma sintering, plasma activated sintering and others, require thermoelectric alloyed powders as raw materials. While the conventional synthetic methods of thermoelectric alloyed materials require very long time of combination reaction due to slow heating and cooling processes. It typically needs a heat preservation of several hours to achieve uniformity of reaction using lower energy density of heat source. Consequently, the balance between performance and fabrication costs plays a vital role in thermoelectric application.

We report a rapid and scalable synthetic method of thermoelectric materials using selective laser melting (SLM) of powder bed with a thickness of 2mm. The mixed powders of thermoelectric element granule in stoichiometric ratio are used as starting materials. Alloy was then formed using SLM method with very high energy density. \( \text{Sb}_2\text{Te}_3 \) bulk with the merit number \( ZT \) at 0.4 was SLM-synthesized. This is comparable with that of the \( \text{Sb}_2\text{Te}_3 \) bulk obtained using conventional melting technology. \( \text{Bi}_2\text{Sb}_3\text{Te}_5 \) bulk was also SLM-synthesized with its \( ZT \) at 0.64. The SLM-synthesized time of thermoelectric materials processed is less than 30 min, compared to tens of hours for conventional melting process. SLM-synthesized method therefore opens up a novel way for rapid, scalable and low-cost manufacturing thermoelectric materials.

Positive and Negative Thermopower by Compositional Tuning of Hybrid Halide Perovskites Md Azimul Haque, Mohammad Insan Nugraha, Sri Harish Kumar Paleti and Derya Baran; KAUST, Jeddah, Saudi Arabia.

Hybrid halide perovskites have recently received exponential interest due to their extraordinary photovoltaic performances.[1] Apart from solar cells, multitude of other applications such as photodetectors, lasers, LEDs, and memory devices have been already demonstrated underpinning the versatile nature of halide perovskites.[2] Despite the unprecedented performance of other hybrid perovskid, their other crucial physical properties such as thermal transports have received limited attention. The majority of the works on thermal transport of hybrid perovskides are accomplished using single crystals or polycrystalline pellets with limited information on seebeck coefficient.[3] Furthermore, in-plane thermal conductivity and seebeck coefficient of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) films remains largely unexplored. Thermal transport behaviors strongly correlate with material structure and its meticulous understanding is imperative for thermal management of efficient and high performance devices. In this work, we systematically investigate the thermal conductivity and thermopower of sequential vapor deposited \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) films. An ultralow in-plane thermal conductivity of 0.3 Wm⁻¹K⁻¹ at room temperature was recorded for \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) using a chip-based \( S \)-method. Temperature-dependent thermal conductivity measurement of a series of \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) films with different degree of methylammonium treatment reveal that the thermal conductivity value is governed by \( \text{PbI}_2 \) octahedron framework. Furthermore, \( n- \) and \( p- \) type \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) films were achieved by compositional tuning of the precursors (\( \text{CH}_3\text{NH}_3 \) and \( \text{PbI}_3 \)) resulting in high positive and negative thermopower. The effect of self-doping and defects on the thermopower along with the implications of the present work on future thermoelectrics based on hybrid perovskides will be discussed.

Performance of an Active Peltier Cooler for Electronics/Batteries Michael J. Adams1, Mark A. Verosky1, Mona Zebjarjadi2 and Joseph P. Heremans1; 1The Ohio State University, Columbus, Ohio, United States; 2University of Virginia, Charlottesville, Virginia, United States.

The design rules for active cooling systems of electronic devices or batteries are quite different from those for Peltier refrigeration. Peltier modules made from tetradymite materials [1] are used commercially for refrigeration, pumping heat opposite the natural direction, but have yet to compete in active cooling where the heat flux from a hot source to a cold sink is the parameter that must be optimized. In particular, a high thermal conductivity is beneficial in the materials used for active cooling, since it allows a higher heat load to be carried away from the device to be cooled, whereas it is obviously detrimental to the \( ZT \) of a Peltier element used in refrigeration mode. The real objective of active cooling is to maximize the effective total thermal conductance, due to both the Fourier and the Peltier heat fluxes, rather than the \( ZT \), which determines the minimum reachable cold temperature in a refrigeration application. Optimal materials for maximum active cooling are those with high thermoelectric power factor and high thermal conductivity [2]. Metals with large thermopower due to magnon drag offer such a prospect. A cooling module is constructed from several possible \( n \) and \( p \)-type metals with high thermoelectric power factor. It is connected so as to pump heat from a variable-power heater into a heat sink. The thermal conductance is first characterized against the temperature gradient in the
absence of a Peltier current (passive cooling mode). It is then characterized again in the presence of an electrical current that maximizes the Peltier heat flux (active mode). The ratio of the thermal conductance of the cooler in active and passive mode is shown as a function of temperature drop and background temperature. The dynamic response is further analyzed and compared to the time constant predicted by thermal resistance and capacitance.


**EPI.13.08.16**

**Developing and Testing of an Experimental Concept of a Hybrid Solar Thermoelectric (HSTE) System**

Paulina V. Escobar, Andrea Arias, Diego I. Oyarzun, Tomas Salinger and Amador M. Guzman; Pontificia Universidad Catolica de Chile, Santiago, Chile; Stanford University, Stanford, California, United States.

In this study, for the first time, we fabricate the thermoelectric mushroom geometry. The model includes Peltier heating at material interfaces and Thomson heating within materials using experimentally measured Seebeck coefficients. The mushroom does not need to be completely amorphized to achieve good memory windows. However, it takes significantly longer times to achieve these operations. Additionally, grain boundary amorphization drastically reduces reset and set times in nanocrystalline GST (down to ~1 ns) as the mushrooms do not need to be completely amorphized to achieve good memory windows.

We measure voltage, current, and temperatures to demonstrate the technical feasibility and performance of the HSTE. Three working fluids were used: deionized water, 10% ethylene glycol and 20% ethylene glycol. The operating characteristic curves are presented under different flow rates in the condensation zone and input powers in the cartridge heater. We found that the best performance occurs for a supplied heat of ~120 W and deionized water as the working fluid. Under this condition, we achieve a maximum of 187.69 mW of electrical power and a maximum of 80.49 W extracted heat in the condenser zone. In general, among the working fluids used deionized water presented the best heat recovery and electricity generation.

In brief, we demonstrate the coupling of a thermosyphon and TE module for heat extraction and electricity generation in a HSTE concept. Future work includes modifications to the system to decrease the energy losses and increase the electricity generation. We also work towards a device that could generate energy for domestic and industrial applications.

**EPI.13.08.17**

**Thermoelectric Properties of Printed Oxide pn Modules**

Yooboon Park, Kyoungah Cho and Sangsik Kim; Korea University, Seoul, Korea (the Republic of).

Oxide materials as thermoelectric materials have been recently researched since they are eco-friendly materials unlike conventional thermoelectric materials such as lead selenide and bismuth antimony telluride. On the other hand, screen printing technique has been widely used for printed electronics. In order to extend the application of oxide thermoelectric devices, it needs to explore the possibility of screen printing process as fabrication technology for oxide thermoelectric pn modules. Hence, we attempt to fabricate square printed oxide pn modules and investigate the thermoelectric characteristics. Herein, we chose n-ZnO and p-Cu2O as representative oxide materials. The ZnO paste was printed on a Si substrate and annealed at 400 °C for 30 minutes before Cu2O paste was printed on the substrate and annealed at 200 °C for 30 minutes. And two Au electrodes (Ea and Ecold) were deposited with an interval of 1 cm. Then the Seebeck coefficients of the n-ZnO and p-Cu2O films were measured.

We use a finite-element PCM model which captures stochastic nucleation, growth, and grain boundary melting to demonstrate thermoelectric effects in a cell with a “double mushroom” geometry. The model includes Peltier heating at material interfaces and Thomson heating within materials using experimentally measured Seebeck coefficients for fcc and amorphous GST (Ge85Sb15), TiN, and SiO2. The double mushroom cell consists of two phase change layers sandwiching an insulating layer which contains a conductive filament. The switching region of the device is in the hearth of the geometry, thermally isolated from the top and bottom contacts by GST layers. This geometry is symmetric and serves as a suitable platform to demonstrate the impact of thermoelectric effects on cell behavior.

Our simulation results show that it is possible to amorphize a single mushroom with lower reset currents (above or below the filament depending on polarity) or two mushrooms both below and above the filament with higher reset currents. Our analysis includes the polarity dependence of both set and reset operations, resistance ratios and the necessary time to achieve these operations. Additionally, grain boundary amorphization drastically reduces set and reset times in nanocrystalline GST (down to ~1 ns) as the mushrooms do not need to be completely amorphized to achieve good memory windows. The crystal grains embedded in the amorphous regions eliminate the need for nucleation, allowing for very fast set but increasing cell-to-cell and cycle-to-cycle variability.


**EPI.13.08.18**

**Thermal Conductivity of Organic-Inorganic Hybrid Perovskite Single Crystals**

Kotaro Matsuyama, Thai Mai H. Doung and Hirokazu Tada; Osaka University, Toyonaka, Japan.

Thermoelectric conversion devices directly convert thermal energy into electricity. In recent years, these devices have received significant attention for their potential to convert waste heat into electricity. Metallic materials like Bi2Te3 with a ZT (figure of merit) value around 1 and a high thermoelectric conversion efficiency, and have been target of research since the 1950s. Despite these efforts, thermoelectric devices are yet to be utilized on a large scale due to their low thermoelectric conversion efficiency and high cost. Hybrid materials utilizing the properties of both organic and inorganic materials have been the subject of many recent studies. Organic-inorganic perovskites have been reported to
have low thermal conductivity and high Seebeck coefficients and are an appealing candidate for use in thermoelectric materials [1],[2]. Various structure of organic-inorganic prepared perovskite. We measured thermal conductivity (k) of these crystals using the steady-state method. We prepared various structures of 1D and 2D single crystals of hybrid perovskites by turning the preparation conditions and organic molecules inserted between the perovskite layer [3]. It was found that a 1D crystal with methyl pyridine showed k of 0.14 (W/mK) while that with pyridine-thiol showed k of 3.3(W/mK). In my presentation, the relationship between the crystal structure and the thermoelectric parameters, and determine the combination that optimizes the thermoelectric conversion efficiency.

References

EP13.08.20
The Role of α- and β- FeSi2 Interfaces on Thermoelectric Properties of Si Rajasekar Parasuraman and Arjun M. Umarij; Materials Research Centre, Indian Institute of Science, Bengaluru, India.

Thermoelectric power generation is a reliable and environmentally friendly technology to convert waste heat into a useful form of energy, which does not involve any moving parts or toxic gas emissions. However, practical application of this technology needs the exploration and development of materials which can be designed, cost-effective and mass produced. Si-based composite materials have been extensively studied for thermoelectric applications because they are cheap, abundant, non-toxic and environmentally friendly. In literature, thermoelectric properties of Si/Ni/Si, Si/β-FeSi2 and Si/CoSi2 composites are studied [1][2].

Si/α-FeSi2 composite has not been studied widely due to metallic nature and the structural transition of α-FeSi2 at 1210 K. However, it is shown in the literature that α-FeSi2 is stable even near room temperatures at Si-rich conditions [3]. Hence, the composite samples of Si/α-FeSi2 and Si/β-FeSi2 have been synthesized by controlling Fe incorporation during mechanical milling. Thermoelectric properties of the samples with α- and β- interfaces have been studied. Si/α-FeSi2 shows higher electrical conductivity and low thermal conductivity, due to the coherency with Si in ‘c’ direction and presence of ‘Fe’ vacancies. This intrinsic ‘Fe’ vacancies act as phonon scattering centers to lower the thermal conductivity. Increased electrical conduction and the reduction in thermal conductivity enhanced the thermoelectric performance of Si/α-FeSi2 composite. Further, Si/α-FeSi2 composites with varying ‘Fe’ vacancy concentration and chemical dopings can be employed to improve the thermoelectric performance.

EP13.08.22
Superior Performance Bi2Te3/PEDOT:PSS Composite for Three-Dimensionally Printed Flexible Thermoelectric Generators Shuping Lin, Wei Zeng, Lisha Zhang and Xiaoming Tao; Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Flexible, lightweight, solution-processible thermoelectric (TE) generators with high room- or low-temperature performance are much desirable in energy harvesting for wearable microelectronics, active microclimate controlling systems and waste heat utilization.[1-3] However, the thermoelectric generators (TEGs) are facing decades of transformation. Up-to-date, there has been a shortage of thermoelectric materials that can be used for such applications. Hooking up these rigid semiconductors to flexible device technology won’t be straightforward.[1-5] To address the problems of the limitation of flexible TE materials, we develop a superior room-temperature performance of Bi2Te3/PEDOT:PSS inorganic-organic thermoelectric composites, which are suitable for printed three-dimensionally flexible thermoelectric generators.[5] For the materials, the Seebeck coefficient of the optimized TE composite is 273.3 μV/K at room temperature, reaching that of pure Bi2Te3, representing the highest value for Bi2Te3/PEDOT:PSS composites reported so far. The corresponding power factor and ZT is 473.5 μW/mK²and 0.4, respectively. Furthermore, the flexible TEGs were fabricated by three-dimensionally 3D printing on aramid paper and PDMS substrates, respectively. The paper-based thermoelectric generator can produce a higher output power of 30.8 mW, specific power density of 12.3 mW/g and areal power density of 20.5 mW/cm²working at under 70 K temperature difference. More importantly, the variation in electric resistance of the PDMS-based flexible TEG is negligible even after 100,000 bending cycles up to 2.5 cm curvature, demonstrating the excellent flexibility and durability of the resultant flexible thermoelectric generator. Therefore, these solution-processible, soft and flexible inorganic-organic composites offer unique advantages that are not available to their rigid counterparts. The methods and findings in this work pave a way to produce high-performance flexible thermoelectric generators for wearable electronic systems, waste heat harvesting and active microclimate control systems.

Acknowledgement
The work has been strongly supported by Research Grants Council of Hong Kong SAR Government (grant no: BBA3) and The Hong Kong Polytechnic University.

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EP13.08.23
Substitutional Effects of Bivalent Zn and Ni Cations on Spin Thermoelectric Properties of Co3O4 Nolan W. Hines1, Gustavo Dans Resende1, Anweeksh Koneru1 and Terence Musho2; 1University of Texas Permian Basin, Odessa, Texas, United States; 2West Virginia University, Morgantown, West Virginia, United States.

Thermoelectric materials show promise in converting waste heat energy in combustion processes to useful energy like electricity. The current low operational efficiencies of thermoelectric materials create difficulties in implementation of these materials for real time applications. Current methodologies such as grain boundary scattering, substitutional effects, band structure engineering, etc., have been utilized to improve the thermoelectric performance, yet have not attained the desired level. An innovative technique is to incorporate these methodologies to semiconducting magnetic thermoelectric materials and extract additional voltage using spin-Seebeck effect, which yields a higher Seebeck coefficient by combining the conversion from conventional charge and spin currents and thus resulting in a higher ZT. Co3O4 is an interesting material with spinel configuration that can allow substitutions with transition metal cations having divalent and trivalent oxidation states. First-principles based density functional theory (DFT) calculations were performed on Zn and Ni substituted Cobalt spinel oxides. The Zn substitution in Co2+ sites resulted in normal spinel structures with no resultant spin polarization, while substituting Cobalt cations with Zn2+ and Ni2+ resulted in a partially inverse spinel configuration with a net resultant spin polarization varying from 0 μB to 4 μB depending on the amount of substitutions. Varying these substitutions alters the spin current due to magnetization fluctuations in the configurational space. DFT calculations executed in quantum espresso were performed on a 56 atom unit cell to find band gap, lattice parameter, effective mass of conduction electrons and spin polarization of each configuration formed with various substitutions of Zn2+ and Ni3+ cations. These fundamental properties were used to perform conventional charge and spin transport calculations by combining non-equilibrium Green’s function approach with spin transport theory to produce a spin transport model. The formalism developed in this research may also be applied to other interesting thermoelectric materials with semiconducting and magnetic properties.

EP13.08.24
Silicides as High Temperature Thermoelectrics for Industry Quansheng Guo, David Berthebaud and Takao Mori; National Institute for Material Science, Tsukuba, Japan.

Thermoelectric power generators are composed of n-type and p-type thermoelectric couples that are connected electrically in series and thermally in parallel and capable of converting heat directly into electricity.[1] The efficiency (h) of thermoelectric power generation technology can be expressed as

\[ h = \frac{\sigma T_c (1 + \alpha T_f)}{\sigma T_c (1 + \alpha T_f) + \sigma T_c (1 + \alpha T_f) T_c / T} \]

where \( T_f \) is hot side temperature, \( T_c \) is cold side temperature and \( z = \alpha a^2 / k \) is the materials’ dimensionless figure-of-merit, where \( a, \alpha, k, T \) refer to the electrical conductivity, Seebeck coefficient, thermal conductivity and the absolute temperature, respectively.[2] Decent performance requires both high electrical transport and low thermal conduction. In addition, thermal stability, machinability, cost and non-toxicity also constitute major issues in thermoelectric devices development.
Considering around 50% of the energy gets lost during its production process and to harvest and convert it into electricity, we focus on materials with potential applications at intermediate-high temperatures. Higher manganese silicides (MnSi2) and iron disilicide (β-FeSi2) are selected as candidates for the p- and n-type legs since both are made of environmentally-friendly and abundant elements. Here we will show the fabrication of thermoelectric devices from silicides with striking thermal stability and attempt to improve the efficiency via reducing contact resistance.

References

EP13.08.25
Reinvestment of the Point Defects in N-Type Bismuth Telluride Based Thermoelectric Materials Qi Zhang, Yehao Wu, Teng Fang, Tiejun Zhu and Xinbing Zhao; Zhejiang University, Hangzhou, China.

The relatively low properties of n-type polycrystalline bismuth telluride based thermoelectric materials, compared to p-type ones, restrict their application in solid state refrigeration. It is the highly random grain orientation and extremely high electron concentration originated from donor-like effect that attributes to the relatively low properties. The former can be realized by applying pressure, while p-type doping and the manipulation of intrinsic point defects are the solution to the latter. For the manipulation of intrinsic point defects, it is well known that the interaction of vacancies with antisite defects, i.e. the donor-like effect, can explain the sharp increase of electron concentration after grinding, pressing and sintering. However, the evolution of the point defects in preparation process remains elusive. In this study, by changing the particle size and hot press temperature, we reinvestigate the intrinsic point defects in n-type bismuth telluride materials. The results show that not only the mechanical deformation, but also the sintering process is vital to the donor-like effect, which is helpful for understanding the nature and evolution of the point defects.

EP13.08.27

Recently, wearable electronic devices are utilized for sensor, heath monitoring and smart gear, etc. However, self-powered supply modules are required for sustainable and battery-free wearable electronics. Therefore, the demand for self-powered supplies for these devices is urgent, and energy-harvesting modules represent a promising method to achieve self-powered electronic systems. Source of renewable energies such as sunlight, wind or human being from human motion and body heat are being studied for the self-power technology. Among these, the human body can be stable and sustained natural heat energy source and temperature difference (ΔT) can be driven between the body heat and ambient atmosphere. Therefore, Thermoelectric (TE) technology, in which energy is harvested from waste body heat, is one of the most suitable candidate technology to operate wearable electronic device. Wearable thermoelectric modules (WTG) is fast becoming a new platform for powering wireless and portable devices. However, we realized that body heat has a limit to obtain a high temperature difference. In previous our study, we obtained a novel cross-plane type of wearable solar TEG (W-STEG) having not only high flexibility but also high performance by integrating solar absorbers on PI substrates. 500nm thick of five-period Ti/MgF2 super-lattice thin film absorbs 96.3% of sunlight in visible light spectrum and ΔT between the hot and cold sides is up to 20.9 °C. The TE legs are prepared by integrating printable BiTe-based TE ink by dispersing mechanically alloy BiTe-based powder and sintering Sb2Te3 and Te in a high viscosity glycerol solvent. In this study, furthermore, we simulated the heat transfer mechanism from the W-STEG module hot side and we proposed the optimal module design to maximize the temperature difference between the hot side and the cold side. We maximize temperature difference between hot side and cold side integrating PDMS cover on solar absorber to block heat convection transfer and attaching flexible copper foam with large surface area which acted as a heat sink. As a result, when exposed to Sunlight, temperature difference between the hot and cold sides was 33.4 °C. The open circuit voltage of the TEG comprising 10 p-n leg pairs is 74.4 mV and the output power is 11.4 μW.

EP13.08.28
Non-Equilibrium Thermal Transport and Thermoelectric Effects at the Melt-Solid Interfaces in Semiconductors Sadid Muneer1, Gokhan Bakanc2, Helena Silva2 and Ali Gokirmak1, 1Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States; 2Electrical and Electronics Engineering, Atılım University, Ankara, Turkey.

Emergence of phase change memory as a viable non-volatile memory technology intensified the interest in high temperature non-equilibrium electro-thermal phenomena at small scales. Phase change memory devices typically operate under large thermal gradients (up to ~50 K/nm) and electrical stresses (up to ~107 A/cm²). The phase change materials transition between the solid and the liquid phases. The general behavior of the phase change devices can be captured by electro-thermal models using temperature-dependent equilibrium values for thermal conductivities, electrical conductivities and Seebeck coefficients1,2. However, as we have observed in our self-heating experiments of silicon microwires, the non-equilibrium processes at the melt-solid interfaces can significantly alter the thermal profiles, hence melting and crystallization dynamics.3 Large number of free electrons and holes are expected to diffuse into the solid material at the liquid-solid interfaces. This injection drastically increases electrical and thermal conductivity due to increased carrier concentrations. Thermal conductivity across the interface is further increased due to heat released by the recombining carriers in the solid. This generation (G) - transport (T) – recombination (R) process (GTR) can be more significant than the electronic convective heat flow by the carriers across the interface. In presence of an electric field at the interfaces, GTR process introduces an asymmetry since minority carriers recombine to release heat if they are drifted into the solid. In a self-heated microwire, this leads to an asymmetric thermal profile that continuously shifts in the direction of the minority carrier flow until a steady state is reached.1,3

References

EP13.08.29
Large Valley Degeneracy and High Thermoelectric Performance in P-Type BaCu₄Ge₄₀₆₈-Based Clathrates Hiroki K. Sato, Hiromasa Tamaki and Tsutomu Kanno; Technology Innovation Division, Panasonic Corporation, Seika-cho, Japan.

There is an increasing interest in high-throughput computational screenings of thermoelectric (TE) materials. A representative example is that valley degeneracy and band effective mass have been demonstrated to be relatively easy to calculate, yet strong descriptors for good electronic properties [1,2]. In this study, we have predicted a high TE performance of p-type BaCu₄Ge₄₀₆₈ based on these descriptors, and experimentally confirmed the prediction. Density functional theory calculations for BaCu₄Ge₄₀₆₈ have found that the stoichiometric compound is a naturally p-doped semiconductor with 6-fold degenerated valleys with light band effective masses. It has also been indicated that introduction of Ge substitutions on the Cu site is effective in controlling the chemical potential. Motivated by these calculation results, a series of Ba₅₋ₓCuₓ₅₋ₓGe₄₀₆₈ samples with different Ge substitution amount x were fabricated by arc-melting and spark plasma sintering, and the transport properties were characterized. It has been observed that the carrier type is effectively controlled with x. The p-type sample with x=0.3 shows a high power factor of ~1 mW/mK², and the thermal conductivity is found to be as low as ~1 W/mK. The resulting TE figure of merit ZT is 0.26 near room temperature, and the peak ZT is 0.62 at 615 K. These ZT values are, although somewhat inferior compared to the record of single-crystalline clathrates (ZT~1.5 at around 500 K [3]), one of the highest among polycrystalline samples (ZT~0.5 at the same temperature range [4]). Therefore, this study further emphasizes the strength of the computational screening in search of high-performance TE materials.
EP13.08.30
Highly Improved Thermoelectric Performance Through Oxygen Manipulation in BiCuTeO
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BiCuTeO is one of the potential thermoelectric materials owing to its low thermal conductivity and high carrier concentration. However, the thermoelectric performance of BiCuTeO is still below average and has a large room for improvement. In this study, we manipulated the nominal oxygen content in BiCuTeO and synthesized BiCuTeO$_{x}$ (x=0.94–1.06) bulk by a solid-state reaction and pelletized them by the cold-press method. The power factor was enhanced via the nominal oxygen deficiency due to the increased Seebeck coefficient. In addition, the thermal conductivity was reduced due to the decrease in lattice thermal conductivity owing to the small grain size that was generated by the deficiency in the nominal oxygen content. Consequently, the ZT value enhanced to around 1.1 at 523 K for the stoichiometric BiCuTeO$_{0.94}$ compared to BiCuTeO. Thus, optimal manipulation of oxygen in BiCuTeO can enhance the thermoelectric performance. This study can be applied to developing the oxides with high thermoelectric performance.

EP13.08.31
High-Throughput Screening of Efficient Bulk and Monolayer Thermoelectric Materials
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National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

While bulk materials are widely used for making thermoelectric devices to convert heat into electricity and vice versa, 2D-monolayers have shown significant potential because of the unique low-dimensional electronic properties. Additionally, although there has been an intensive work in systematic high-throughput discovery of new bulk thermoelectric materials, similar investigations for monolayer and their comparison to bulk materials is still in the developing phase. In this work, we identify both bulk and monolayer thermoelectric materials using semiclassical transport method with density functional theory. We emphasize on inclusion of proper units of thermoelectric properties especially for monolayer materials because of their surface nature rather than bulk 3D nature. We establish the correlations in thermoelectric properties of monolayer materials and their bulk counterparts. We find the density of state at the Fermi-level to be correlated with Seebeck coefficient behavior for both bulk and monolayers. We also show the periodic trends, crystallographic and compositional trends for the whole dataset. After screening a few candidate bulk and monolayer materials, we carry out higher-level Green function based approaches to calculate more reliable thermoelectric properties of the screened materials. We made our results publicly available through NIST’s JARVIS-DFT database (http://jarsv.nist.gov) consisting of more than 3000 bulk and 700 monolayer materials.

EP13.08.32
High Thermoelectric Efficiency in Monolayer PbI$_2$ from 300 K to 900 K
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By using a first-principles approach, monolayer PbI$_2$ is found to have great potential in thermoelectric applications. The linear Boltzmann transport equation is applied to obtain the perturbation to the electron distribution by different scattering mechanisms. The mobility is mainly limited by the deformation-potential interaction with long-wavelength acoustic vibrations at low carrier concentrations. At high concentrations, ionized impurity scattering becomes stronger. The electrical conductivity and Seebeck coefficient are calculated accurately over various ranges of temperature and carrier concentration. The lattice thermal conductivity of PbI$_2$, 0.065 W/mK at 300 K, is the lowest among other 2D thermoelectric materials. Such ultrathin thermal conductivity is attributed to large atomic weight, weak interatomic bonding, strong anharmonicity, and localized vibrations in which the vast majority of heat is trapped. These electrical and phonon transport properties enable high thermoelectric figure of merit over 1 for both p-type and n-type doping from 300 K to 900 K. A maximum ZT of 4.9 is achieved at 900 K with an electron concentration of 1.9×10$^{13}$ cm$^{-2}$. Our work shows exceptionally good thermoelectric energy conversion efficiency in monolayer PbI$_2$, which can be integrated to the existing photovoltaic devices.

EP13.08.33
Fabrication of Thermoelectric Devices with High Aspect Ratio Pillars by Using Patterned Electro-Chemical Deposition in Multi-Channel Glass Template
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Thermoelectric (TE) devices, which can realize the mutual transformation between heat and electricity directly both in “Seebeck effect” and “Peltier effect”, have attracted worldwide interest because of their promising widely applications in electronics, for example airspace part, local refrigeration, accurate temperature controlling and telecommunications components. Compared with traditional energy conversion components, TE devices are superiorly applicable to the applications where weight and size are limited because they could be operated under small temperature difference produced by small energy sources and could apply well to low power levels. Therefore, the integration and miniaturization of the thermoelectric devices is becoming a top issue to promote its materialization combining with micro-electromechnanical systems(MEMS) and integrated circuit (IC) technology. The thermoelectric couples of the TEG fabricated by mechanical cutting and array configuration is difficult to reach micron scale for it is limited by processing technology. To solve this problem, template forming method was used in fabricating thermoelectric device in order to achieve high integration and aspect ratio in finite area for it’s unique advantage that it can utilize chemical self-assembly technology combing with MEMS technology. After manufacturing some vertical hole arrays in the template, TE materials were filled in the micro-pores by electrodeposition. This work demonstrates that micro thermoelectric generators (TEGs) with large output power of 218 μW and output voltage of 34.7 mV under a larger temperature difference of 98 K can be fabricated using electro-deposition based on the multi-channel glass template, which is much higher than the reported works. The micro-TEGs was consisted of four pair of thermocouples. And each thermocouple was composed by about two hundred p-type legs of Sb2Te3 and two hundred n-type legs of Bi2Te3 with 60 μm in diameter and 200 μm in height, which are well filled in the glass template by impulse voltage deposition.

EP13.08.36
Enhanced Thermoelectric Properties of N-Type Bi$_2$Te$_3$-Based Materials
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A thermoelectric figure of merit ZT has been mainly improved by reducing thermal conductivity, resulting record high performance in several important thermoelectric (TE) systems. Their thermal conductivity rapidly approaches to the amorphous limit. In contrast, power factor (PF) does not have the theoretical upper bound, and it directly determines the output power of TE modules. However, enhancing PF is highly challenging, especially for Bi$_2$Te$_3$-based compounds that are representative TE materials near ambient temperature. Here we report ultrahigh power factor and carrier mobility in new n-type Bi$_2$Te$_3$-based materials, which are stabilized under excess Cu and Te conditions. The enhanced power factor is attributed to markedly high carrier mobility and electrical conductivity, which increase with the higher extent of Cu.

EP13.08.37
Enhanced Thermoelectric Performance of Highly Crystalline Ge$_{1-x}$Sb$_x$Te Crystals
Tianwey Lan, Min-Nan Ou, V.K. Ranganayakulu, Shih-Hsun Yu and Yang-Yuan Chen; Academia Sinica, Taipei, Taiwan.

Pristine GeTe is a highly degenerate semiconductor shows very low thermoelectric properties due to its large carrier concentration induced by the presence of Ge vacancy. In this work, we report a promising thermoelectric figure of merit (zT) of ~1.8 at 700–740 K was obtained on high-quality Ge$_{1-x}$Sb$_x$Te crystals grown by the Bridgman method. The substitution of Sb into Ge sub-lattice significantly reduces the excess hole concentration due to the donor dopant nature of Sb. The zT enhancement can be attributed to the reduction of carrier density due to Sb doping, as well as optimizes the electrical conductivity which subsequently enhances the Seebeck coefficient in Ge$_{1-x}$Sb$_x$Te compared to the pristine GeTe crystal. Reduction of thermal conductivity arises from enhancing phonon scattering by Sb doping effect, which results indicate that Sb doping is effective for enhancing the thermoelectric performance in p-Type GeTe Compound. With the inelastic neutron scattering investigation of selected Ge$_{1-x}$Sb$_x$Te crystals, the significant difference on phonon dispersion relation is investigating.
EP13.08.38

Electron-Phonon Interactions in Normal and Inverse Nickel Substituted Cobalt Spinel Oxides
Gustavo Damis Resende¹, Nolan W. Hines¹, Anveeksh Koneru² and Terence Musho²; ¹University of Texas at the Permian Basin, Odessa, Texas, United States; ²West Virginia University, Morgantown, West Virginia, United States.

Harvesting waste heat from power plants and other sources has proven to be a great challenge. Though thermoelectric technology has the capability to directly convert waste heat energy to electricity, the strong association of electrons and phonons in thermoelectric materials is greatly hampering the field. This research studied the electron-phonon interactions in spin-polarized materials formed by substitutions of Ni⁰ in Co₃O₄ spinel matrix. The preferential substitution of Ni⁺ in the octahedral sites changes to tetrahedral interactions with the increasing concentration of Ni⁺ resulting in the transition from inverse spinel to a partially inverse spinel. This change in the preferential substitution also accompanied a sudden change in spin-polarization, band gap, effective mass and lattice parameter. Thorough ab-initio studies were performed on a 56 atom unit cell of three configurations: inverse spinel \([\text{Co}_3\text{Ni}_x\text{O}_4 (0<x<0.5)]\), normal spinel \([\text{Co}_3\text{Ni}_x\text{O}_4 (0<x<1)]\) and partially inverse spinel \([\text{Co}_3\text{Ni}_x\text{O}_4 (0<x<0.5)+\text{Ni}_y\text{O}_2 \text{Co}_{2-y} \text{O}_3 (0<y<0.5)]\). These interactions were tuned by substitutions to attain optimal thermoelectric performance while extracting additional voltage associated to the spin of electrons in the spin-polarized materials. When the spin-polarization of the material is maximized, the spin thermoelectric module takes advantage of the spin Seebeck effect to generate extra voltage even when the electronic and thermal conductivities are not at their respective optimum levels. In an ep spin thermoelectric material configuration, the contributions of conventional and spin thermoelectric modules were combined to yield a higher operational thermoelectric efficiency.

EP13.08.39

Effect of Annealing on Thermoelectric Characteristics of Ag₃Te Nanoparticle Thin Films
Seunggeen Yang, Kyongha Cho and Sangsig Kim; Electrical Engineering, Korea University, Seoul, Korea (the Republic of).

Recently, energy conversion from heat to electricity has emerged in the field of energy devices. Solution-processable thermoelectric nanoparticles (NPs) have been considered as promising materials for high efficient thermoelectric devices on flexible plastic substrate. Nevertheless, the low electrical conductivity of NPs acts as a barrier to the development of high efficient NPs-based thermoelectric devices. Hence, in this study, we attempt to increase the electrical conductivity of Ag₃Te NPs thin films through annealing below plastic deformation temperature and investigate the effect on the thermoelectric characteristics. Ag₃Te NPs were synthesized in an aqueous solution by the colloidal method. To examine the thermoelectric characteristics of the Ag₃Te NPs thin films, a platform consisting of a meander line patterned heater and two electrodes at a distance of 40 μm was prepared on a plastic substrate by a photolithography and sputtering method. A heater and two electrodes were made of Pt, and the Ag₃Te NPs thin film was formed between the two electrodes by spin-coating. The Ag₃Te NPs thin film was annealed at 150 °C by rapid thermal annealing in vacuum. Irrespective of whether an Ag₃Te NPs thin film is annealed or not, the thermoelectric characteristics show p-type behavior. The Seebeck coefficients of non-annealed and annealed Ag₃Te NPs thin films are 1740 and 1260 μV/K, respectively. On the other hand, the electrical conductivities of non-annealed and annealed Ag₃Te NPs thin films are 0.16 and 11 S/m, respectively. Owing to annealing, the electrical conductivity of the Ag₃Te NPs thin films increases by about 100 times. Considering that low electrical conductivity of the NPs thin films results from poorly connected NPs in the thin film, it implies that annealing process makes strong connection between NPs in the thin film. With the Seebeck voltage and the electrical conductivity, we calculate the output power of non-annealed and annealed Ag₃Te NPs thin films. The values of non-annealed and annealed of the Ag₃Te NPs thin films are calculated to be 0.69 and 79.1 μW/cm² at a temperature difference of 7.5 K, respectively.

EP13.08.40

Development of Novel Eutectic Thermoelectric Alloy Systems and the Effect of Directional Solidification
Srisaha P; Indian Institute of Science, Bangalore, India.

Conversion of dissipated heat into electricity is the basic principle of thermoelectricity. It has wide variety of applications in the areas such as automobile engineering, refrigerating coolants, satellite etc. In search of such materials thermoelectric has gone wide scope to complex materials like Tellurides, Clathrates, Zinc compounds, Half Heusler alloys, Si, Ge, Skutterudite etc. The defining factor for thermoelectric materials is ZT, thermoelectric figure of merit. This attributes to the power factor \(P=\sigma S\), the electrical and thermal conductivities, and the absolute temperature, respectively. The thermal conductivity is a combination of thermal conductivity via electrons, \(\lambda_e\), and phonons, \(\lambda_p\), i.e., \(k=\lambda_e+\lambda_p\). The main difficulty in improvement of the efficiency of a thermoelectric device is due to the complex relation between \(\sigma, \alpha\) and \(k\). Improving the transport properties correlation will be presented.

EP13.08.41

Developing an Optimized Preparation Process for Bi₂Te₃-Se₅ Based Alloys for Thermoelectric Power Generation Applications
Omer Meroz and Yaniv Gelbstein; Ben Gurion University of the Negev, Beer Sheva, Israel.

The thermoelectric method of directly converting thermal into electrical energy is attracting increased attention for such applications and thus enhancing its efficiency is of great importance. The performance of thermoelectric devices is assessed by the dimensionless figure of merit \(ZT\) of the material, defined as \(ZT=\alpha^2\sigma/k\), where \(\sigma\), \(\alpha\) and \(k\) are the Seebeck coefficient, the electrical and thermal conductivities, and the absolute temperature, respectively. The thermal conductivity is a combination of thermal conductivity via electrons, \(\lambda_e\), and via phonons, \(\lambda_p\). The main difficulty in improvement of the efficiency of a thermoelectric device is due to the complex relation between \(\sigma\), \(\alpha\) and \(k\). Improving the performance of thermoelectric materials is usually done either by improving the power factor, \(P=\sigma S\), or by applying phonon scattering methods in order to lower the thermal conductivity. The most efficient n-type thermoelectric materials for temperatures up to 300°C are currently Bi₂Te₃-Se₅ based. By optimizing the preparation process while considering the inherent characteristics, an even more dramatic, the efficiency of such materials can be further improved. In this study the Bi₂Te₃-Se₅ composition was optimized by CH₂ doping, preferred alignment of the crystallographic orientation, and lattice thermal conductivity minimization. The synthesis route included rocking furnace melting, ball-milling or melt spinning, and hot pressing with optimal parameters for enhancement of the thermoelectric figure of merit, \(ZT\), at temperatures higher than 200°C, commonly applied in low temperature power generation applications. The transport properties in the directions parallel and perpendicular to the pressing direction were examined. In the direction perpendicular to the pressing axis, a maximal \(ZT\) of ~0.9 was obtained at ~175°C and at ~210°C, which is as far as we know among the highest ever reported for n-type Bi₂Te₃-Se₅ based alloys.

EP13.08.42

Conduction Band Engineering and Phonon Softening for High Performance N-Type PbSe Thermoelectrics
Chongjian Zhou¹,² and In Chung¹,²; ¹Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul, Korea (the Republic of); ²School of Chemical and Biological Engineering, Seoul, Korea (the Republic of).

PbSe is an attractive tellurium-free thermoelectric material for the intermediate temperature power generation. However, the performance of PbSe is much poorer than its more expensive isostructural analogue of PbTe. Here we present that PbSeSnₓBrx0.002-2xCuxSe exhibits peak ZT 1.8 at 723 K and average ZT 1.1 between 300 and 823 K, which are the highest values to date for all previously reported n- and p-type PbSe-based materials as well as for tellurium-free n-type polycrystalline materials. Cu:Se doping simultaneously flattens the conduction band edge of PbSe, increasing the effective mass of charge carriers, and band gap, which substantially improves the Seebeck coefficient. It also raises the carrier concentration with a negligible damage in carrier mobility, thereby even improving the electrical conductivity above ~423 K. These induced factors synergistically result in
ultrahigh power factor, reaching $\sim 21 - 26 \mu W cm^{-1}K^{-2}$ over a wide range of temperature from $\sim 423$ to $723$ K. Cu$_2$Se doping markedly depresses the lattice thermal conductivity to $\sim 0.4$ W m$^{-1}K^{-1}$ at $773$ K, which is close to its theoretical amorphous limit. First-principles calculations show that the obtained ultralow value originates from the remarkable softening of acoustic phonon at the low-frequency region.

Solid-state thermoelectric technology uses electrons or holes as the working fluid for heat pumping and power generation and offers the prospect for novel thermal-to-electrical energy conversion technology that could lead to significant energy savings by generating electricity from waste industrial heat. The key to the development of advanced TE technologies is to find highly efficient TE materials. Recently, several novel concepts have been proposed to enhance the efficiency of TE materials and laboratory results suggest that high $zT$ values can be realized in several families of bulk materials. In this presentation, we will show the study on the thermoelectric properties of liquid-like materials. We will show these materials possess interesting thermoelectric properties with ultralow thermal conductivity and good thermoelectric figure of merit. The physical mechanisms behind these abnormal thermoelectric properties will also be discussed. Finally, the stability of these compounds will also be presented and discussed.

In this presentation, the results and outcome of a 3-year project aiming at discovering new TE materials will be discussed, shown and critically analyzed.

Among the emerging promising thermoelectric materials is AgBiSe$_2$. This class of materials shows an intrinsically low lattice thermal conductivity stemming from a strong anharmonicity of the Bi$^{5+}$ lone pair. AgBiSe$_2$ crystallizes in a trigonal structure at room temperature. At 460 K the structure changes into a rhombohedral structure and at 580 K to a cubic rock salt structure. At the same time, AgSbSe$_2$ crystallizes in a rock salt cubic structure without any phase transitions.

In this work, we show the influence of the vacancy and Sb substitution on the structure and thermoelectric properties in Ag$_{1-x}$Bi$_x$Se$_2$ and Ag$_{1-x}$Sb$_x$Se$_2$. Synchrotron Bragg and pair distribution function analyses show the existence of site-disorder between Bi and Ag at room temperature, induced by the phase transitions during cooling. While the site-disorder leads to enhanced point defect scattering, the vacancy doping shows that the site-disorder can be mitigated. Furthermore, we will show how the substitution using Sb influences the phase transition temperature, local and with it the thermal transport. These studies show the direct effect of defects and the local structure on the transport in thermoelectric materials.

Prior ultralow thermal conductivity materials are not suitable for thermoelectric applications due to the limited electronic transport in the materials. Here, we present a new class of ultralow thermal conductivity materials with substantial electronic heat transport. Our samples are graphene/metal heterostructures of transferred graphene and ultrathin metal films (Pd, Au and Ni) deposited by either thermal evaporation or rf magnetron sputtering. For the evaporated samples, we achieve an ultralow thermal conductivity of 0.06 W m$^{-1}K^{-1}$. We attribute the electronic contribution to the transmission of electrons across atomic pinholes in graphene. With the ultralow thermal conductivity and substantial electronic transport, the new materials could be explored for thermoelectric applications.

The identification of effective approaches to significantly increase the power factor in thermoelectric materials could lead to substantially improved thermoelectric performance. In this context, modulation doping, in which the pathways for transport of charge are spatially separated from the dopant ions, has witnessed a rebirth in interest. Enhanced power factors have recently been reported in multilayer bulk nanoparticle composites, attributed to improved carrier mobilities without degradation of the Seebeck coefficient. While attractive from a device perspective, such materials can be challenging to model and experimentally characterize in order to understand the detailed charge transfer and transport processes, due to a distribution of grain sizes with random relative crystallographic orientations, and ill-defined microstructures. In contrast, precisely layered composites with well-defined layer thicknesses and compositions are ideal systems for the fundamental study of such phenomena. Here we use simple single band and composite models to predict the thermoelectric properties of modulation-doped layered composites. In particular, we have modeled the charge transfer and transport processes in layered composites comprised of doped and undoped layers, including the effects of ionized impurity and deformation potential (acoustic phonon) scattering. The potential for thermoelectric power factor enhancement in such structures will be discussed.
Nowadays, it seems to be a great majority of people that energy needs to be generated, conserved, and recycled in better ways. We need to prevent as much as possible to waste it, since every joule saved means less fossil fuel burnt. Because of that harvesting waste energy are becoming a popular among the scientific community. And, one of the most promising approaches is nano-engineering thermoelectric materials to produce devices. Thermoelectrics are a class of materials able to convert wasted heat energy into electricity. By controlling nano-structured properly, their efficiency increase. And, since the devices have no moving parts, they are extremely reliable. In this talk, different approaches to nanostructure different materials will be shown and how those approaches help to increase the final efficiency of the material and the final device. I will show three recent examples: selenides of Ag and Cu done with our recent development Pulsed Hybrid Reactive Magnetron Sputtering (PHRMS), large area antioide bismuth tellurides, and a three-dimensional interconnected bismuth tellurides nanowires array.

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A Ruiz-Clavijo, O Caballero-Caler, M Martin-Gonzalez “Three-Dimensional Bi2Te3 Networks of Interconnected Nanowires: Synthesis and Optimization” Nanomaterials, 2018, 8 (5), 345.
Thermoelectric materials directly convert heat into electricity and vice versa.

A large variety of thermoelectric materials' classes including, intermetallic compounds (e.g. half-Heuslers), silicides and chalcogenides (e.g. Bi\(_2\)Te\(_3\), PbTe and GeTe), have been investigated as candidates for practical applications due to high thermoelectric figure of merit, ZT, values at different temperature ranges.

In the recent years, many of the advances of improving the ZT and thereby enhancing the heat to electricity conversion efficiency, have been focused on generation of nano-features, effectively scattering phonons, for minimization of the lattice thermal conductivity. Yet, such nano-domains are in many cases unstable under the high temperatures operating conditions, tending to grow into the micro-meter scale, while degrading the ZT.

Moreover, the effect of grains- and/or domains boundaries and their high temperature variations on the electronic properties is rarely considered.

In the current presentation, the govern temperature dependent physical metallurgical effects on the ZT, will be described in details, with some innovative approaches for mitigating these adverse effects, by means of thermodynamically driven phase separation and grain boundary Zener pinning effects. In addition, the effect of these and other metallurgical factors (e.g. vacancies and dislocations) on the electronic transport properties will be presented.

A focus on the related activities in the Department of Materials Engineering at Ben-Gurion University of the Negev will be given.

2:15 PM EP13.10.03
Combined Theory and Data-Driven Approaches Thermoelectrics Materials Discovery Ambabray Jain\(^1\), Alireza Faghaninia\(^1\), Alexander Ganose\(^1\), Vahe Tshityouni\(^1\) and Gerbrad Ceder\(^1,2\)
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We describe our efforts to discover new thermoelectric materials compositions through a combination of theory and data-driven approaches. In particular, we focus on two efforts. The first is a new model of carrier transport called AMSET that allows one to model the temperature-dependent Seebeck coefficient and mobility from first-principles at reasonable computational cost. This is achieved by adapting classical scattering equations previously developed for 1D parabolic band semiconductors to complex density functional theory band structures. We will explain the theory behind AMSET as well as comparison against experiment and constant relaxation time approaches typically used in the field. Next, we will describe our data-driven approach to suggest new thermoelectric compositions. This effort leverages a corpus of over 3.3 million abstracts of materials science journal articles that we have collected, and for which we have used natural language processing techniques to extract the correlation between a material's composition and its likelihood to be a thermoelectric based on automatically "reading" the prior literature. We demonstrate that this technique can potentially predict new thermoelectric materials years in advance of their first report in the scientific literature and explain the manner in which this machine learning model arrives at predictions. For both methods, we present comparisons to the experimental data, both previously tabulated and conducted with our collaborators for new materials.

2:30 PM EP13.10.04
Electron-Phonon Coupling and Electronic Transport in N-Type PbTe from First Principles Jiang Cao\(^1\), Jose D. Querales-Flores\(^1\), Aoife R. Murphy\(^2\), Stephen Fahy\(^2\) and Ivana Savic\(^3\)
\(^1\)Tyndall National Institute, Cork, Ireland; \(^2\)University College Cork, Cork, Ireland.

Exploiting the fascinating properties of materials near soft mode phase transitions is an emerging concept in the quest to increase thermoelectric efficiency [1]. Soft phonons may lead to low thermal conductivity, while preserving high electronic conductivity. Here we investigate the unusual electronic transport properties of n-type PbTe, which is a classic thermoelectric material that exists near a soft mode phase transition. Our first principles calculations show that longitudinal optical phonon scattering dominates electronic transport, while acoustic phonon scattering is relatively weak [2,3]. We find that scattering due to soft transverse optical phonons is by far the weakest scattering mechanism, due to the symmetry-forbidden scattering between the conduction band minima and the zone center soft modes [3]. Soft phonons thus play the key role in the high thermoelectric figure of merit of n-type PbTe: they do not degrade its electronic transport properties although they strongly suppress the lattice thermal conductivity [1].


This work was supported by Science Foundation Ireland under Investigators Programme No. 15/IA/3160.

2:45 PM EP13.10.05
Structural and Electronic Properties of Ferroelectric Domain Walls in GeTe from First Principles Djordje Dangic\(^1\), Eamonn Murray\(^2\), Stephen Fahy\(^2\) and Ivana Savic\(^3\)
\(^1\)Tyndall National Institute, Cork, Ireland; \(^2\)University College Cork, Cork, Ireland; \(^3\)Imperial College London, London, Ireland.

Domain walls in ferroelectric oxides can have significantly different properties than their bulk counterparts [1]. This represents a new avenue for the manipulation of material properties for specific purposes. GeTe is a ferroelectric material that is also one of the best performing thermoelectrics, combining beneficial electronic properties with low lattice thermal conductivity [2] and mechanical stability [3]. In this work, we have performed first principles calculations to understand how domain walls affect structural and electronic properties of GeTe. We have identified five different types of domain walls. We find that strong strain-order parameter coupling is present at all of them, which is beneficial for the thermal conductivity and mechanical stability [2,3]. We will explain the theory behind AMSET as well as comparison against experiment and constant relaxation time approaches typically used in the field. Next, we will describe our data-driven approach to suggest new thermoelectric compositions. This effort leverages a corpus of over 3.3 million abstracts of materials science journal articles that we have collected, and for which we have used natural language processing techniques to extract the correlation between a material's composition and its likelihood to be a thermoelectric based on automatically "reading" the prior literature. We demonstrate that this technique can potentially predict new thermoelectric materials years in advance of their first report in the scientific literature and explain the manner in which this machine learning model arrives at predictions. For both methods, we present comparisons to the experimental data, both previously tabulated and conducted with our collaborators for new materials.


This work is supported by Science Foundation Ireland PI Award 15/IA/3160.

3:00 PM BREAK

3:30 PM *EP13.10.06
Defective Half-Heusler Thermoelectric Compounds with Intrinsic Vacancies Tiejun Zhu; Zhejiang University, Hangzhou, China.

Typical 18-electron half-Heusler (HH) compounds, ZrNiSn and NbFeSb, have been identified as promising high temperature thermoelectric materials. NbCoSb with nominal 19 valence electrons, which is supposed to be metallic, has recently been reported to also exhibit thermoelectric properties of a heavily doped n-type semiconductor. In this talk we experimentally demonstrate that the nominal 19-electron NbCoSb is actually the composite of 18-electron Nb\(_{3+}\)CoSb (0 ≤ d ≤ 0.05) and impurity phases. Single phase Nb\(_{3+}\)CoSb with intrinsic Nb vacancies, following the 18-electron rule, possesses improved thermoelectric performance, and the slight change in the content of Nb vacancies has a profound effect on the thermoelectric properties. The carrier concentration can be controlled by varying the Nb deficiency, and the optimization of the thermoelectric properties can be realized within the narrow pure phase region. Benefiting from the elimination of impurity phases and the optimization of carrier concentration, thermoelectric performance is remarkably enhanced by ~100%. The similar phenomenon has also been observed in some of other defective 19-electron HH compounds. This work opens a new avenue for searching for nominal 19-electron half-Heusler compounds with intrinsic vacancies as promising thermoelectric materials.

4:00 PM EP13.10.07

Typical 18-electron half-Heusler (HH) compounds, ZrNiSn and NbFeSb, have been identified as promising high temperature thermoelectric materials. NbCoSb with nominal 19 valence electrons, which is supposed to be metallic, has recently been reported to also exhibit thermoelectric properties of a heavily doped n-type semiconductor. In this talk we experimentally demonstrate that the nominal 19-electron NbCoSb is actually the composite of 18-electron Nb\(_{3+}\)CoSb (0 ≤ d ≤ 0.05) and impurity phases. Single phase Nb\(_{3+}\)CoSb with intrinsic Nb vacancies, following the 18-electron rule, possesses improved thermoelectric performance, and the slight change in the content of Nb vacancies has a profound effect on the thermoelectric properties. The carrier concentration can be controlled by varying the Nb deficiency, and the optimization of the thermoelectric properties can be realized within the narrow pure phase region. Benefiting from the elimination of impurity phases and the optimization of carrier concentration, thermoelectric performance is remarkably enhanced by ~100%. The similar phenomenon has also been observed in some of other defective 19-electron HH compounds. This work opens a new avenue for searching for nominal 19-electron half-Heusler compounds with intrinsic vacancies as promising thermoelectric materials.

4:00 PM EP13.10.07
Many new thermoelectric materials including half-Heusler alloys, PbTe and SnSe based compounds, skutterudites, clathrates, to a name a few, are known to possess rich and complex bandstructures, with highly anisotropic bands belonging to multiple valleys having manifold degeneracies in both conduction and valence bands. These materials often exhibit very low thermal conductivities, which can be further reduced using nanostructuring techniques to reach down to, or even below the amorphous limit. More recently, however, significant efforts are also being undertaken to take advantage of the rich bandstructure features to achieve power factor improvements as well. These include identifying the best alloying strategies, introducing resonant states in the bands, aligning of the bands, matching of the valleys at the same energy, etc. Large efforts are also placed by the computational materials science community into bandstructure calculations through involved DFT codes and high-throughput material screening using data from a variety of databases.

Less progress, however, is achieved in combining such involved calculations with accurate transport models, which take into account different scattering mechanisms including their energy dependences, the details of intra/inter valley scattering, details of anisotropy in the bandstructure, electronic relaxation details, etc. Lack of these considerations leads to wrong performance estimations, inaccurate comparisons, and sub-optimal design directions. At the moment, most calculations, despite the use of accurate bandstructures, are performed using constant relaxation time approximation due to the very challenging computational complexities of accurate scattering treatment.

Here, we describe the development of an advanced simulator that uses an arbitrary material bandstructure and computes the thermoelectric coefficients beyond the typically assumed constant relaxation time approximation. Our code includes all major scattering mechanisms (e.g., phonons, impurities, alloying) encountered in the materials of interest. The code uses the Fermi’s Golden Rule in the energy dependent relaxation time approximation, computed by numerical considerations of all bandstructure states. Using this, we then report on an investigation of a few typical thermoelectric materials and explore the differences in the performance predictions in cases where the various details of the scattering mechanisms as described above are considered in the calculations, versus if they are omitted using simplified methods. We indeed show that depending on the scattering physics considered, the power factor can vary substantially and materials performance rankings can be altered. More specifically, we show that in the efforts towards improving the power factor of materials through band alignment, different optimized bandstructure conclusions are reached if one uses the constant relaxation time approximation, versus scattering rates that depend on the density of intra-valley states, versus scattering rates that depend on the total density of states. In the case of half-Heusler compounds, for example, we show that the differences in the performance estimation of band aligned structures can vary significantly depending on the scattering mechanism. We show that this variation depends on the effective masses of the aligned bands of the material as well.

Finally, we discuss the numerical issues of these simulations and approximations that could speed up the computation significantly without compromising the accuracy.

Organic/inorganic thermoelectric nanocomposites (TENCs) have seized great attention since they integrate the advantages of inorganic (high electrical conductivity) and organic (low thermal conductivity and mechanical flexibility) parts. Major barriers obstructing the development of this field are the lack of n-type TE materials and the absence of precise control of the morphology directly relevant to TE performance. To resolve these two issues, here we provide a feasible strategy to improve the blend film morphology of n-type TENCs consisting of organic polymer and inorganic metallic nanofiller.

As proof-of-concept, we utilized the magnetic characteristics of cobalt nanowires (Co NWs) to direct the assembly of metallic nanowires in an insulating polyvinylidene fluoride (PVDF) matrix through solution fabrication method. The resulting highly ordered n-type TENCs exhibit significantly increased electrical conductivities (σ) in comparison to randomly packed nanowires. It is interesting to note that the s and Seebeck coefficient (S) of these TENCs are decoupled, which is consistent with the n-type metallic behavior of Co. Both s and S simultaneously increase as a function of the Co NWs content. As a result, the maximum power factor (PF) of 523 μW m−1 K−2 is obtained at 320 K with 45 vol% Co NWs under magnetic alignment, which is among the highest PFs achieved for n-type TENCs. Importantly, these TENCs are highly bendable and thus hold great potential for flexible TE modules. By pairing these n-type TENCs with p-type PEDOT:PSS thin films, we constructed bendable and planar TE generators that produce a maximum output voltage and power of 26.4 mV and 5.2 μW, respectively, when temperature gradient reaches 50 K.

Furthermore, we employed n-type conducting polymer N2200 to replace insulating PVDF in the above TENCs and aimed to understand the favorable contributions of organic semiconductor to the charge carrier transport process. Distinct from Co NWs/PVDF counterparts, Co NWs/N2200 TENCs exhibit the intimately coupled s and S and the highest PF up to 288 μW m−2 K−1 is acquired with 31 vol% Co NWs. Despite extra conductive pathways are anticipated to create in Co NWs/N2200 TENCs relative to PVDF based analogues, the s is undermined by the unsatisfactory porous microstructures in thin films, presumably caused by the rigid molecular chains of N2200 compared to flexible PVDF. To enhance the interconnectivity between Co NWs and N2200, a small amount of PEI-treated n-type single-walled carbon nanotubes (SWCNTs) were added to the optimal binary sample. The s of ternary TENCs increases and then drops with the addition of SWCNTs, yielding an optimal PF as high as 384 μW m−2 K−2 at 380 K at the content of 3 wt% SWCNTs.

**References**


**4:45 PM EP13.10.08** Impact of Scattering Mechanism Details on the Thermoelectric Power Factor of Complex Materials *Patrizio Grazioso, Chathurangi Kumarasinghe and Neophyto Neophytou; School of Engineering, University of Warwick, Coventry, United Kingdom.*

In this work, electrical and thermal properties of semi-metallic ZrTe2 and TiSe2 were calculated, and its thermoelectric properties assessed.

Half-Heusler thermoelectric materials have attracted much attention due to their high thermal stability, mechanical strength, power factor (PF) and figure-of-merit (ZT) at high temperatures. In order to translate the material performance into good module performance, electrical and thermal contact resistances must be minimized. Low electrical contact resistance between electrode and thermoelectric material is critical for device performance. Poor contacts can cause Joule heating which can significantly degrade the power output. Ideally, the contact resistivity should be smaller than 1 μΩ cm². In practice, many material systems are far from achieving this resistivity value. In this study, we demonstrate a half-Heusler thermoelectric module with excellent contact resistance and thereby excellent module performance. The contact resistivity was measured using a scanning probe measurement system, and specific resistivity at each interface was calculated. A very low contact resistivity of ~1 μΩ cm² was achieved resulting in power output close to theoretically predicted value. This device fabrication technique provides pathway for high temperature power generation technology in waste heat recovery.
Thermoelectric effects for Heat-to-electricity conversion are fascinating phenomena with many potential technological applications from waste heat energy harvesting, IR camera, e-skin to interactive buildings. We give an overview of those phenomena in electronic or ionic conducting polymers. In the first part, we summarize our finding on the electronic thermoelectric properties of the p-type polymer called poly(3,4-ethylenedioxythiophene) (PEDOT) [1]. PEDOT thermoelectric aerogels are presented with their applications in dual pressure and temperature sensors [2]. We then focus on the recent advances made in the lab regarding n-type conducting polymers [3].

In the second part, we explore the ionic thermoelectric effects in both mixed ionic electronic polymer conductors [4]. This phenomenon is used to create materials orthogonal sensitive to humidity, temperature and pressure.

In a third part, we investigate on ionic polymer transistors. Giant Seebeck effects are found with coefficients that reach 10 mV/K. This effect enables charging a supercapacitor for energy harvesting of intermittent heat sources; but also switching a transistor, thus creating a smart pixel for high temperature sensitivity [5]. The concept of non-ionic aqueous thermoelectric polymers is further explored to obtain both negative and positive ionic Seebeck coefficient and build the first ionic thermopiles.


9:15 AM EP13.11.02 Enhanced Thermoelectric Performance of PEDOT:PSS Nanotubes via AAO Template-Assisted Growth [Hyejeong Lee] 1, Ho Shun Shin 2, Taejin Yoo 1, Seonmin Jin 1, Byoung Hun Lee 1, Jae Yong Song 2, Eun Ji Lee 1 and Ji Young Jo 1; 1Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); 2Center for Nanomaterials Characterization, Korea Research Institute of Standards and Science, Daejeon, Korea (the Republic of).

As smart devices have become an integral part of our lives, there is a growing demand for the development of self-charging devices that can simultaneously generate and store energy. Among them, thermoelectric generator (TEG) are noiseless and can be miniaturized easily. Conducting polymers are the appropriate choice for wearable thermoelectric devices among TEGs, due to their flexibility, eco-friendliness, lightweight, etc. Poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been widely studied owing to its highest electrical conductivity (> 10 Scm -1) with low thermal conductivity (< 1 Wm -1K -1). However, the thermoelectric efficiency of PEDOT:PSS is still low due to the low electrical conductivity and Seebeck coefficient, compared to the inorganic materials. Here we present a strategy to enhance the electrical conductivity and to decrease the thermal conductivity simultaneously, in order to achieve the high thermoelectric efficiency of PEDOT:PSS. We successfully fabricated PEDOT:PSS nanotubes with an average diameter of 200 nm via infiltration in AAO template without any synthesis process. From the transmission electron microscopy (TEM) and Raman spectra, the infiltration method using the capillary phenomenon forms a PEDOT:PSS nanotube with a wall thickness of 10 nm and induces a stretching in the PEDOT:PSS C=C–C=C bond with a linear alignment. We found the increase in electrical conductivity due to stretching of PEDOT:PSS chains as well as the decrease in thermal conductivity through phonon scattering at the inner and outer interfaces of the nanotube.

At first, the PEDOT:PSS solution was dropped on to the AAO template and PEDOT:PSS solution was infiltrated into AAO template for 24 hr at room temperature. Then the sample was baked at 120°C to remove residual solvent followed by Ethylene glycol treatment for 120 min for improving the electrical conductivity of PEDOT:PSS nanotubes. The samples were then rinsed and then baked at 120°C for 10 min. The AAO barrier layer was removed by immersing the template in NaOH followed by vacuum filtering. The PEDOT:PSS nanotubes were then collected from NaOH solution. We believe that the fabrication process of PEDOT:PSS nanotubes using a facile infiltration method not only enhances the thermoelectric efficiency but also helps us in understanding the thermoelectric behavior at lower dimensions.

9:30 AM EP13.11.03 Organic Micro Thermoelectric Generators for Waste Heat Energy Harvesting Matteo Massetti 1, 2, Silvio Bonfadini 1, 2, Luigino Crisante 1, Mario Caironi 1 and Marco Cussignelli 1; 1Istituto Italiano di Tecnologia, Milano, Italy; 2Politecnico di Milano, Milano, Italy.

Micro energy harvesters are becoming more and more relevant as energy resources for distributed low power electronics and sensors networks. In this context, micro thermoelectric generators (µTEG) possess many advantages, as they can be worked in the dark and require limited maintenance. Ideally, such µTEGs should be cost effective and based on abundant materials. Organic conjugated materials have been studied to address such requires, as they can enable lightweight, flexible and cost competitive µTEGs produced through mass scaled printing techniques. Here we report on a new organic, flexible µTEG where doped p-type and n-type organic semiconductors are inkjet printed to form a micro module composed of 128 thermocouples on plastic. In particular, we will present an architecture specifically devised to improve the thermal coupling and simplify the fabrication process. Our successful realization of a printed organic µTEG and the complete thermoelectric characterization allow to envisage future efficient devices delivering µW/cm 2 at low average temperature and low temperature differences.

9:45 AM EP13.11.04 The Role of Polymer Structure on N-Type Organic Thermoelectrics Suhao Wang 1, Hengda Sun 2, Tim Erdmann 2, Daniele Fazzi 2, Magnus Berggren 1, Xavier Crispin 2, Anton Kiriy 2, Tobi J. Marks 2, Antonio Facchetti 1 and Simone Fabiano 1; 1Linköping Univ, Norrkoping, Sweden; 2Technische Universität Dresden, Dresden, Germany; 3Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany; 4Northwestern University, Evanston, Illinois, United States.

Organic thermoelectric based on conjugated polymers are emerging as promising candidate for green energy conversion. Building such devices require both p-type (hole-transporting) and n-type (electron-transporting) materials. Although p-type polymers can efficiently be doped to exceptionally high electrical conductivity (σ) values (>1000 Scm -1) with low thermal conductivity (< 1 Wm -1K -1), the development of n-type polymer lags far behind due to their low conductivity (typically <0.01 S/cm). For example, it has been shown that the naphthalenediimide–bithiophene copolymer P(NDI2OD-T2), a high electron mobility polymer extensively investigated as active layers in OPET/OSC devices, can be doped to a conductivity of only 0.003 S/cm regardless of the dopant and processing conditions.

Recently, we demonstrated that the twisted donor-acceptor structure of P(NDI2OD-T2) can lead to strong charge carrier intrachain localization on the acceptor moiety, thus resulting in low electron conductivity. On the other hand, backbone planarization can be beneficial for charge carrier delocalization, enhancing the charge transport and the extent of the doping process. To this end, we replaced the bithiophene (T2) unit in P(NDI2OD-T2) with the more electron-deficient bithiazole (Tz2) unit, resulting in the analogous P(NDI2OD-Tz2). Hereby, the polymer donor-acceptor character can be reduced and the lower intrachain steric helps planarize the polymer backbone and thus enhancing intermolecular π–π stacking interactions, with consequently a much higher electrical conductivity (up to ~0.1 S/cm) and enhanced thermoelectric response. These results demonstrate how significantly the polymer backbone structure affects the polaron delocalization and the resulting n-doped conductivity, setting molecular-design guidelines for the next generation of conjugated polymers.

10:00 AM BREAK

10:30 AM EP13.11.05 Improved N-Type Doping and Thermoelectric Properties of a Polymer Semiconductor by Minimizing Donor-Acceptor Character Jian Liu 1, Yongjiang Shi 2, 1; Jingjin Dong 1, Xinrui Qu 1, 2; Ryan Chiechi 1, Giuseppe Portale 2, Mengyao Sc 4, Xugang Guo 2, 3 and Lambert Jan Anton Koster 1; 1Zernike Institute for Advanced Materials, University of Groningen, University of Groningen, Groningen, Netherlands; 2Department of Materials Science and Engineering and The Shenzhen, Southern University of Science and Technology (SUSTech), Shenzhen, China; 3Stratingh Institute for Chemistry, University of Groningen, University of Groningen, Groningen, Netherlands; 4Kee Key Laboratory for Printed Organic Electronics, Southern University of Science and Technology (SUSTech), Shenzhen, China.

Organic semiconductors have attracted increasing attention as low-temperature thermoelectric materials, offering the possibility of fabricating low-cost, large-scale and mechanically flexible thermoelectric modules. The thermal conductivity of organic semiconductors is intrinsically low, leaving the power factor as the most important parameter for optimization. A widely used strategy to optimize power factor is molecular doping, which enables a tuning of the carrier density in organic films. Fine tuning of the electronic properties of donor-acceptor (D-A) copolymers can be readily fulfilled via meticulous selection of the two moieties, which affords substantial electron mobilities >1 cm 2V -1 s -1 in organic thin-film transistors. However, translating those high electron mobilities of D-A copolymers into high electrical conductivities upon n-doping is nontrivial and has rarely been successful to date. The weak n-doping of D-A copolymers limits their use in organic thermoelectrics.
Thin films are fabricated by spin coating technique using a yellow solution of MASnI thin films baked at 100°C shows the best result with Seebeck coefficient about 70 μV/K and electrical conductivity of about 50 S/cm near room temperature. The detailed results and analysis will be shown during the presentation. In future, our plan is to optimize the carrier concentration to enhance the value of ZT.

References:
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SESSION EP13.12: Thin Film, Device and Others
Session Chairs: Theodor Kyrtidis and Takao Mori
Friday Afternoon, April 26, 2019
PCC North, 200 Level, Room 225 A

1:30 PM *EP13.12.01 Development of Thermoelectric Thin Films for IoT and Characterization Methods Takao Mori1; 2; CFSP and WPI-MANA, National Institute for Materials Science (NIMS), Tsukuba, Japan; 1University of Tsukuba, Tsukuba, Japan.

There is a vital need to develop technologies to dynamically harvest energy from surroundings to power IoT applications [1]. In regards to utilizing ubiquitous thermal energy like body heat, thermoelectric thin films can be promising [2]. Recently, we have utilized semiconductor fabrication processes to fabricate an organic n-type thermoelectric module outputting over 250 mV with 80°C [3]. The high contact resistance and relatively low thermoelectric performance of the organic materials used, remains a large issue to solve. I will mainly present efforts on developing inorganic thermoelectric thin films, which can be applied to wearable applications via flexible substrates, for example. We have also discovered that utilizing magnetism can be a way to enhance thermoelectric properties, e.g. magnetic semiconductors [4]. There is a possibility to compatibly integrate such thermoelectrics into magnetic devices and sensors to self-power themselves. Development of measurements to accurately evaluate the thermal conductivity of thin films and
interfacial thermal resistance are also vital. We have recently developed a novel TEM in-situ thermal probe, which utilizes nanothermocouples with scanning heat input under STEM, to be able conduct nanoscale heat maps which visualize the heat pathways in nanocomposite materials and in-plane of thin films, for example [5]. Focused picosecond thermoreflectance with advanced analytic methods to enable unambiguous, accurate measurements and evaluation of interfacial thermal resistance will also be presented. CREST, CSFN, WPI-MANA project collaborators are acknowledged.

References

2:00 PM EP13.12.02
Solution-Processed PbSe\(_{1-x}\)Te\(_x\) Thin-Films Thermoelectrics Prathamesh B. Vartak, Zhongyong Wang, Yuanyu Ma and Robert Wang; Arizona State University, Tempe, Arizona, United States.

Solution processing of inorganic semiconductor precursors and its subsequent thermal decomposition offers a simple, inexpensive, large area fabrication route to inorganic semiconductor thin films. However, the presence of inherent strong covalent bonds renders these inorganic semiconductors insoluble. Hydrazine as an example is known to form soluble metal chalcogenide precursors but its high toxicity, explosive and carcinogenic nature inhibits its widespread application. Diamine-dithiol solvent mixture was discovered recently to dissolve a variety of metal chalcogenides. This solvent system poses problems of introducing sulfur contamination in metal selenides and tellurides, the presence of free tellurium in metal tellurides, and immediate precipitation of PbTe precursors.

We propose a new approach to prepare metal chalcogenide precursors by mixing elemental metal with diphenyl dichalcogenide in a variety of solvents.2 This approach simultaneously avoids hazardous solvents, eliminates unwanted sulfur and free tellurium impurities, and yields lead selenide and telluride precursors that have been problematic via other soluble precursor syntheses. We characterize the thermal decomposition temperature of the precursors using thermogravimetric analysis and confirm the formation of phase-pure metal chalcogenides using powder X-ray diffraction. We also characterize the chemical structure of a PbSe precursor made in this manner due to its potential thermoelectric applications. We identify the PbSe precursor to be lead(II) phenylselenolate by utilizing a combination of techniques including nuclear magnetic resonance, mass spectrometry, elemental analysis and single crystal X-ray diffraction analysis.

We further prepare PbSe\(_{1-x}\)Te\(_x\) thin films by decomposing a mixture of lead selenide and lead telluride precursors and present their room temperature Seebeck coefficient and electrical conductivity. In addition, we introduce Na dopants by including NaCl into the precursor mixture and systematically study its influence on the thermoelectric properties of PbSe\(_{1-x}\)Te\(_x\) thin films. The film stoichiometry and electronic state of elements were characterized by Rutherford backscattering spectroscopy and X-ray photoelectron spectroscopy. We also use secondary ion mass spectroscopy depth profiling to confirm the presence of Na-dopants in our thin films. The room temperature measurements seem to be promising with undoped PbSe\(_{1-x}\)Te\(_x\) films having Seebeck coefficient of 480 μV K\(^{-1}\) and electrical conductivity of 180 S m\(^{-1}\). Since PbSe\(_{1-x}\)Te\(_x\) is best suited for high-temperature applications, we also present our ongoing efforts to measure the thermoelectric properties of these samples at high temperature.

References:

2:15 PM EP13.12.03
Flexible Aerosol Jet Printed Thermoelectric Films via Versatile Photonic Sintering Mortorza Saeidi-Javash, Chaochao Dun, Wenzheng Kuang, Nicholas Kempf and Yanliang Zhang, Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana, United States.

Additive printing is a promising method to fabricate flexible and low-cost thermoelectric devices using high-performance colloidal nanocrystals. However, most of the TE nanoparticles require sintering at elevated temperatures, which poses a major challenge to print and sinter the TE nanoparticles on low-temperature flexible substrates.

In this work, we demonstrate for the first time the aerosol jet printing combined with intense pulsed light (IPL) sintering to transform colloidal TE nanoparticles into high-performance and flexible thermoelectric films. This paves the way for roll-to-roll fabrication of printed TE generators with high power density on a large variety of low-temperature substrates. The conventional thermal sintering process requires long heating time, and is limited to substrates that can survive high temperatures. The IPL sintering is an ultrafast thermal sintering method using a xenon flash lamp to deliver a high-intensity and short-duration (< 2 ms) pulsed light to the printed nanoparticles. By controlling the pulse intensity and duration, the IPL sintering can effectively sinter the printed nanoparticles without overheating or damaging low-temperature substrates.

We printed n-type bismuth telluride based TE films on flexible substrates such as kapton and PET and sintered the films by IPL. The sintering parameters were optimized in order to achieve the highest electrical conductivity and maximum thermoelectric power factor. The electrical conductivity of the flexible films is dramatically improved from non-conductive to 2.7×10\(^4\) S/m, which results in a very high power factor of 726 μW/mK\(^2\) at room temperature. The aerosol jet printing and IPL sintering process is fully roll-to-roll compatible, thus providing a highly-scalable and low-cost manufacturing method to fabricate flexible TE devices for broad energy harvesting and cooling applications.

2:30 PM EP13.12.04
Uni-Leg Thermoelectric Module Comprised by Coated Hybrid-Pervoskite Thin Film Shrikanth Sanj, Tomohide Yabuki and Koji Miyazaki; Mechanical and Control Engineering, Kyushu Institute of Technology, Kitakyushu, Japan.

The conversion efficiency of thermoelectric material is quantified by figure of merit ZT (=\(\sigma S^2/\kappa\)) where \(\sigma\) is electrical conductivity, \(S\) is Seebeck coefficient and \(\kappa\) is thermal conductivity. CsSnI\(_3\) pervoskite can lead to the next-generation energy conversion platforms due to its intrinsic ultra-low thermal conductivity and large Seebeck coefficient.

However, enhancement of electrical conductivity is still required.

In this work, we study the growth parameters and thermoelectric properties of coated CsSnI\(_3\) pervoskite thin film. Our focus is to develop these thin films by cost-effective wet printing process for large area application. Due to shapeability thin films are superior to the corresponding bulk or single crystals. Here, we fabricate CsSnI\(_3\) pervoskite thin film by spin coating process. The base solution is prepared by CsI and SnI\(_2\) precursors. We optimized the effects of mixing time, baking temperature and baking time to evaluate and enhance thermoelectric performance of CsSnI\(_3\) thin films. CsSnI\(_3\) thin films were structurally characterized using several state of the art techniques including XRD and SEM. We measured thermoelectric properties near room temperature and found that growth parameters influence the crystal grain size further the value of figure of merit. CsSnI\(_3\) thin films grown at solvent mixing time about 2 h, heating temperature about 130°C and heating time 5 min show the best thermoelectric performance as Seebeck coefficient 100 μV/K, electrical conductivity 30 S/cm, thermal conductivity 0.4 W/mK, and ZT about 0.1 near room temperature.

Further, we fabricated uni-leg thermoelectric modules on a glass substrate comprised by the best grown CsSnI\(_3\) thin film. Number of legs varies from 3 to 5 in our study. The maximum output power is about 0.8 nW for 5 legs (25 mm x 3 mm x 500 nm) module for temperature difference of about 3°C. Even though output power is low but these results will open a new pathway to thermoelectric modules for flexible electronics. In future, our plan is to optimize the module design and transfer it to flexible and large area substrate.

2:45 PM EP13.12.05
Solid state thermoelectric coolers (TEC) made from nanostructured materials have received attention for Peltier cooling of localized hotspots in microprocessors (1, 2). Research in this area has focused on steady-state operation and cooling. Here, we discuss a concept for pulsed-mode transient heat spreading using planar thin film TEGs. Using detailed computational modelling, we show that it is possible to achieve a local cooling of ~10°C for a high heat flux of 1000 W/cm² by optimizing the TEC material, geometry and operating parameters. We experimentally investigate ultra-thin films of (Bi$_2$Sb$_3$Se$_2$): system of compounds as a viable candidate for such operation. Typical room temperature electrical resistivity of these samples is around 300 μΩ·cm (3). Excellent electrical contacts can be made, as well, with typical values ranging between 10-8 and 10-9 Ω·cm. We report measurements of the thermoelectric properties of few-qnt-perlament Bi$_2$Se$_3$ on sapphire substrate to provide insight into alteration of properties at few-atomic layer scales. This work explores new ideas for TEC operation in handling transient temperature jumps in electronics.


3:00 PM BREAK

3:30 PM *EP13.12.06

Origin of High Thermoelectric Performance in n- and p-Type SnSe Crystals Li Huang; Department of Physics, Southern University of Science and Technology, Shenzhen, China.

Tin selenide (SnSe) has emerged as a very promising thermoelectric material due to its record high figure of merit ZT for both n- and p-type crystals in intermediate temperature range. In this talk, I will present our recent works regarding its electronic and thermal properties based on first-principles calculations, in combination with the Boltzmann transport theory and experimental measurements. The origins of strongly anisotropic thermal and electrical behaviors in this layered lattice structure will be discussed, which give rise to the highest optimal ZT values along the a (out-of-plane direction) in the n-type SnSe, whereas along b axis in p-type materials. In addition, I will discuss the effects of the intrinsic defects and dopants on its thermoelectric characteristics. Our calculations show reasonable agreements with the experimental observations and provide some guidance for optimizing the thermoelectric performance.

4:00 PM EP13.12.07

Optimization of Thermoelectric Materials and Devices for Self-Powered Wearable Health and Environmental Tracking Systems Abhishek Malhotra$^1$ and Daryoosh Vasheae$^1$; $^1$Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina, United States; $^2$Material Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States.

There has recently been an increasing interest in self-powered wearable health and environmental monitoring systems. The Advanced Self-Powered Systems of Integrated Sensors and Technologies (ASSIST) at North Carolina State University, is a prime example of the thrust for these systems. Thermoelectric generators (TEG) can continuously harness the body heat and produce electricity, as such they are the promising candidates for making battery-less wearable systems. Several challenges need to be addressed before TEGs can power such wearables. Particularly, the thermoelectric material properties must be optimized so that the material is most efficient near the body or room temperature. Bi-Sh-Te-Se nanocomposite alloys are known as the state-of-the-art thermoelectric materials for near room temperature applications; however, the existing materials have their peak ZT in the temperature range of 100 °C to 150 °C with smaller values near the body temperature. These nanocomposites often also suffer from lack of reproducibility due to the difficulties in controlling the Te vacancy during the material synthesis. Metalization of these materials for making the TEGs poses other requirements such as durability to survive in the regular usage. Another essential element imposed by the low-temperature differential on the body is related to making thin and long TE legs and low fill factor devices. The integration in textile or wearable bands also dictates certain design restrictions to make reliable devices for body heat harvesting. In this study, we will describe our methods to address some of these issues starting from the material synthesis, device design, and TEG fabrication to integration in wearable testbeds. An extensive investigation was performed on doping optimization and reproducibility of the nanocomposite bismuth telluride based alloys especially n-type materials which are more sensitive to growth process parameters. The effects of Cu doping for synthesizing a reproducible n-type material with high ZT near room temperature was investigated. The peak ZT of 1.2 at room temperature was achieved. Reproducibility of the material was confirmed through tight statistical analysis. For p-type material, Bi-Sh-Te nanocomposites were synthesized with peak ZT of 1.4 near room temperature. Furthermore, physical and chemical processing methods were tested for surface preparation before metallization.

4:15 PM EP13.12.08

Interfacial Patterning as a Framework for Creating High ZT Thermoelectric Materials Shane G. Davies$^1$, Duncan Hardie$^2$, Francis H. Davies$^1$, Ned T. Taylor$^1$, Conor J. Price$^1$ and Steven P. Hepplestone$^1$; $^1$Department of Physics and Astronomy, University of Exeter, Exeter, United Kingdom; $^2$Deregallera Ltd, Caerphilly, United Kingdom.

With ~60% of all generated energy wasted as heat[1], energy harvesting is an important avenue to help provide for our worlds increased power demand in a sustainable way. Thermoelectric (TE) devices offer the unique opportunity to recover this previously wasted energy, and improve performance, via a direct conversion of heat to electricity in a solid state device. The key limitation of TE devices is their poor power conversion efficiency, characterised by the dimensionless figure of merit, ZT. This value depends on both the electron and phonon transport characteristics, which themselves are heavily interdependent. For optimal TE behavior the electronic conductivity should be high whilst the thermal conductivity is kept to a minimum. However, in the majority of cases an increase in electrical conductivity is accompanied by an increase in thermal conductivity due to the Wiedemann-Franz Law[2], which links the thermal conductivity of electrons to the charge carrier density. It is this interdependence which has effectively limited the maximum ZT achievable to its current value of ~3[3]. Therefore, the ideal technique for raising ZT further would break this interdependence and optimize these characteristics independently. With this in mind, we investigate interfacial patterning as a method for controlling the transport properties of phonons. This method utilizes the fundamental difference in electron and phonon wavefunctions to selectively scatter phonons and hence reduce thermal conductivity, whilst having a minimal effect on electronic transport. Using density functional theory, we demonstrate the effectiveness of interfacial patterning on Si/Ge structures. We investigate three differently patterned interfaces, noting how subtle changes in the patterning can have dramatic effects on properties such as the effective mass and the lattice thermal conductivity. This patterning provides a technique to enhance ZT and a framework for producing more viable devices from any heterostructure-based TE materials.

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4:30 PM EP13.12.09

Thermal Transport in Electrodeposited Antimony Telluride Films of Varying Silver Content Laia Ferrer-Arregui$^1$, Zini Yu$^1$, Jiwon Kim$^2$, Nosang Myung$^3$, Jae-Hong Lim$^2$ and Jacho Lee$^1$; $^1$Mechanical and Aerospace Engineering, University of California, Irvine, Irvine, California, United States; $^2$Electrochemistry Research Group, Materials Processing Division, Korea Institute of Materials Science, Changwon-si, Korea (the Republic of); $^3$Department of Chemical and Environmental Engineering and UC-KIMS CIME, University of California-Riverside, Riverside, California, United States.

While electrodeposited antimony telluride thin films with silver demonstrated promising thermoelectric properties, their thermal conductivity and the silver-content-dependence remain unknown. Here we report the thermal conductivity of Ag$_x$(Sb$_{1-x}$Te$_2$) and AgSbTe$_2$ thin films with controlled annealing and temperature conditions and demonstrate the impact of silver content on thermal transport. By annealing the as-deposited samples at 160 °C, the room-temperature thermal conductivity of Ag$_x$(Sb$_{1-x}$Te$_2$) and AgSbTe$_2$ films increases from 0.24 to 1.59 Wm$^{-1}$K$^{-1}$ and from 0.17 to 0.56 Wm$^{-1}$K$^{-1}$, respectively. When the pre-annealing temperature is below 110 °C, the thermal conductivities of the films are lower compared with the Sb$_2$Te$_3$ films (undoped) treated by identical annealing conditions. The thermal conductivity increases are attributed to the crystal growth, which are...
supported by the estimated grain size based on X-ray diffraction analysis. The thermal conductivity reduction of silver-doped films compared with the undoped films is attributed to the inhibited nucleation and crystallization of Sb$_2$Te$_3$ especially for films annealed below 110 °C, supported by the transient thermal conductivity measurement at 94 °C which reveals the crystallization activation energy to be 1.14 eV and 1.16 eV for Ag$_{18}$Sb$_{48}$Te$_{63}$ and AgSbTe$_2$ films, respectively. By increasing the pre-annealing temperature, we observe competing effects between the amorphous and crystalline phases in the silver-doped samples, confirmed by the temperature-dependent thermal conductivity measurement and the semi-empirical models combining different phonon scattering mechanisms. Based on previously reported electrical data, we estimate the room-temperature thermoelectric figure of merit of Ag$_{18}$Sb$_{48}$Te$_{63}$ and AgSbTe$_2$ to be 0.95 ± 0.35 and 0.71 ± 0.07. These results improve our understanding of the role of metal doping in thermal transport, which can guide optimal designs of chalcogenide materials for room-temperature thermoelectric applications.

4:45 PM EP13.12.10
Thermoelectric Figure-of-Merit of Polycrystalline P-Type Doped SiGe Thin Films Mohammadali Esfamisary, Yingying Zhang, Xiaojia Wang and Uwe Kortshagen; Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

Silicon-germanium (SiGe) thin films are low cost and low toxicity candidates for high temperature thermoelectric applications. Thin films of p-type boron doped amorphous SiGe are deposited on quartz substrates via Plasma Enhanced Chemical Vapor Deposition (PECVD). This plasma uses RF powers of 1-10 W with pressures of 220 - 400 mTorr. The substrate is heated to 250°C during the film growth, which improves the quality of the film by providing the atoms with sufficient mobility to find a more stable and lower defect configuration. Boron is used as the dopant with concentrations ranging from 0.5% to 15%. By 15 minutes deposition, thin films with thicknesses of 250 - 400 nm are produced. Post deposition, polycrystalline structure is obtained by thermal annealing of the samples at 650°C for 10 hours. Raman spectroscopy shows three peaks for Ge-Ge, Si-Ge, and Si-Si bonds in both amorphous and polycrystalline films with higher intensities for the latter. This confirms higher crystallinity of the polycrystalline films compared to the initial amorphous samples. The thermoelectric figure-of-merit (ZT) is calculated by the conductivity and thermopower measurements at room temperature. The dark conductivity and Seebeck coefficient are measured in a vacuum chamber and the thermal conductivity is obtained by the ultrafast laser pump-probe technique. The effect of varying doping level, RF plasma power, and Ge concentration on the power factor of thin films is studied. The characterization is performed at two points in the process, pre- and post-annealing. The power factor is highly dependent on the doping concentration in both cases with a peak at the mid-range doping concentration. This is mainly due the balance of the carrier density and carrier mobility in doped samples. Results also show a minimum of three orders of magnitude improvement of the thermoelectric figure-of-merit after annealing in all conditions.

This work is supported by the Minnesota Environment and Natural Resources Trust Fund (ML 2016, Chp. 186, Sec. 2, Subd. 07b).

SYMPOSIUM ES01

Organic Materials in Electrochemical Energy Storage
April 23 - April 26, 2019

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* Invited Paper

SESSION ES01.01: Redox Organic Electrolyte Materials in Aqueous Organic Redox Flow Batteries I
Session Chairs: Tianbiao Liu and Qing Wang
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 126 A

10:30 AM *ES01.01.01
Recent Progress in Organic-Based Aqueous Flow Batteries Michael J. Aziz; Harvard University, Cambridge, Massachusetts, United States.

The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity generation from intermittent renewable sources such as wind and solar. Wide-scale utilization of flow batteries is limited by the cost of redox-active metals such as vanadium or precious metal electrocatalysts. We have developed high performance flow batteries based on the aqueous redox behavior of small organic and organometallic molecules, e.g. [1-8]. These redox active materials can be very inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling massive electrical energy storage at greatly reduced cost. We have developed new protocols for measuring capacity fade rates and have discovered that the capacity fade rate is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed [7]. We will report the performance of the very few chemistries with long enough calendar life for practical application in stationary storage.


http://dx.doi.org/10.1002/aenm.201702056
Until very recently, the choice of electroactive materials in aqueous RFBs has been limited mostly to transition metal redox species, such as all-vanadium RFBs, which however are limited by the high cost of vanadium. Aqueous soluble organic (ASO) redox-active materials have recently shown promise as alternatives to transition metal ions to be employed in RFBs because of structural tunability, cost-effectiveness, availability, and safety features. To date, reported research on ASO species is rather limited and has been focused mostly on quinone, viologen, TEMPO, and ferrocene compounds.

In this presentation, we describe development of a new high energy density organic redox material as a promising ASO anolyte. In our research, we focused on investigating the primary ASO properties (i.e., solubility and redox potential) through a framework of combined nuclear magnetic resonance (NMR), density functional theory (DFT), organic synthesis, and electrochemical studies. Rational introduction of functional moieties in an asymmetrical configuration initiates preferential solvation that significantly enhances the solubility from near-zero to up to 1.8 M in potassium based supporting electrolyte. The electrochemical performance of the new organic redox couple based anolytes was evaluated in a RFB using the well-established ferro/ferricyanide catholyte that leads to a high cell voltage of 1.4 V. Cycled at a high ASO concentration of 1.4 M (96 % of its maximum solubility of 1.45 M in 1 M NaOH ), the flow battery produced an exceptional reversible volumetric capacity of 67.4 Ah L⁻¹ demonstrating for the first time of a ASO redox active material with reversible capacity equivalent to 2.8 M electron concentration.


**References**


**SESSION ES01.02: Redox Organic Electrolyte Materials in Aqueous Organic Redox Flow Batteries II**

**Session Chairs: Michael Aziz and Song Jin**

**Tuesday Afternoon, April 23, 2019**

**PCC North, 100 Level, Room 126 A**

**1:45 PM *ES01.02.01**

**Soluble, Stable Organic Redox-Active Materials for Redox Flow Batteries**

**Xiaoliang Wei**
Pacific Northwest National Laboratory, Richland,Washington, United States.

Redox flow batteries (RFBs) are an exciting target for storing renewable energy at a large scale. Currently available commercial RFBs relying on vanadium as the redox material have suffered from high cost to be scale to a grid-level size. Such a challenge could be reduced if redox-active organic molecules could be used instead of vanadium. In addition, the design of redox molecules with various functionalities can tune the molecular properties, which eventually allows for improving the solubility and controlling the redox potentials to optimize their performance. However, there are very few candidates that could serve as organic redox materials and almost all of them act as a single-electron carrier. For increasing the energy density, the effective strategies are (1) increasing voltage gap as the redox materials reversibly respond more negative/positive potentials for negolyte/posolyte, respectively, (2) increasing solubility, and (3) designing redox materials capable of two (or more)-electron storage, which instantly doubles the energy density. Here we present some research results which have been done in our laboratory for the target of increasing energy density. We show a new class of organic material of naphthalene diimide (NDI) that can reversibly store two electrons at neutral pH in aqueous solution. By decorating with glycinate, the solubility of n-type organic semiconducting NDI was improved in aqueous solution. We studied the fundamental two-electron redox behavior from experimental and computational analyses and displayed a prototype RFB containing [K-BNDI] negolyte and 4-OH-TEMPO posolyte with reasonable cyclability, energy efficiency and excellent stability. To improve the stability of redox materials, we also attempted to use redox-active organometalllic molecules such as pseudo-octahedral Co-polypyridyl complexes, and developed rational strategies for enhancing the robustness, namely, the spin-crossover between low and high-spin states and the chelation effect emerging from replacing three bidentate ligands with two tridentate analogues.

**References**


**2:15 PM *ES01.02.02**

**Sulfonate Functionalized Viologens for Energy Storage with Superior Energy Density and Cycling Stability**

**Jian Lu**
Bo Hu, Camden Debruler, Maowei Hu, Wenda Wu and Tianbiao L. Liu; The Department of Chemistry and Biochemistry, Utah State University, Logan, Utah, United States.

To efficiently utilize the intermittent renewable energy source such as wind and solar energy and achieve sustainable society, advanced large-scale energy storage technologies are highly demanded. Among various energy storage devices, aqueous organic redox flow batteries (AORFBs) are one of the most promising battery technologies for large scale storage of intermittent energy because of a number of technological merits including decoupled energy and power, higher current and high power performance, safety features, and synthetic tunability of charge storage molecules. Herein, we developed a serial of low-cost, highly water soluble sulfonate functionalized viologens as anolyte for AORFB.
applications. The negative charged sulfonate pendant side chains and favorable molecular sizes of these viologens enable their compatibility with cation exchange membranes. The newly designed viologens were paired with low-cost I$_2$/Br$_2$/Br and Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ catholytes in RFBs using cation exchange mechanism. The 1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium, (SPr)$_2$V/I RFB delivered 1.0 V battery voltage and reliable battery performance under a pH neutral condition. When the (SPr)$_2$V was paired with a newly designed organometallic catholyte material (NH$_4$)$_2$Fe(CN)$_6$, a 0.9 M pH neutral (SPr)$_2$V/Fe(CN)$_6^{3-}$ system delivered unprecedented storage capacity and cycling stability, specifically, 24.1 Ah/L electrolyte capacity, 62.6% energy efficiency and 100% capacity retention in 1000 cycles (more than 45 days testing duration), which represents the best cycling stability among all reported organic RFBs. To further improve battery voltage and energy density, the (SPr)$_2$V was paired with Br$_2$/Br catholyte. The (SPr)$_2$V/Br RFB delivered a battery voltage of 1.51V, 78% energy efficiency, and up to a 30.4 Wh/L operated energy density in a 1.5 M battery. Other asymmetric sulfonate functionalized viologens, such as (Se)$_2$(SPr)$_2$V and (SPr)$_2$(SBu)$_2$V, with even higher chemical stability and water solubility were also prepared for AORFB applications.

The urgent need for cleaner energy technologies calls for a radical change in the energy mix to favor renewable energy (+138.5 GW added in 2016 [1]) and environmentally responsible energy storage solutions. Within this background, the development of reliable, efficient, low-polluting and low-cost electrochemical storage systems can be considered as particularly important. Among the various possible technologies, Redox Flow Batteries (RFBs) is believed as suitable devices for large-scale energy storage [2]. Basically, both physico-chemical and electrochemical properties of the selected redox-active species are particularly crucial. Thus their solubility, chemical stability and the resulting output voltage (after assembly) define the energy density, the cyclability and the power density of the system, respectively. Interestingly, the use of organic electroactive species enable access to low cost and possibly greener compounds because composed of naturally abundant elements. Moreover, they offer high structural designability through the well-established principles of organic chemistry and notably access to both n- and p-type electrochemical storage mechanisms [3–5]. As part of our ongoing effort in developing novel Aqueous Organic Redox Flow Batteries (ORFBs), we will present our recent results dealing with the synthesis and characterizations of a novel highly soluble organic derivative used as catholyte and based on the stable tetramethylpiperidine N-oxyl moiety [6,7]. The electrochemical properties of the catholyte will be reported as well as additional data obtained in a full battery configuration.

References


Song Jin; University of Wisconsin–Madison, Madison, Wisconsin, United States.

Due to the intermittent nature of sunlight, practical solar energy utilization systems demand both efficient solar energy conversion and inexpensive large scale energy storage. We have developed novel hybrid solar-charged storage devices that integrate organic redox flow batteries (RFBs) and regenerative semiconductor solar cells that share the same pair of redox couples. In these integrated solar flow batteries (SFBs), solar energy is absorbed by semiconductor electrodes and photoexcited carriers are collected at the semiconductor-liquid electrolyte interface and used to convert the redox couples in the RFB to fully charge up the battery. When electricity is needed, the charged up redox couples are discharged to generate the electricity. We have demonstrated that solar energy harvest, conversion, storage, and redelivery can be completed by such a single integrated SFB without any external electrical energy input. After developing high performance III-V solar cells that are carefully matched with various high voltage organic couples and optimizing several generations of SFB device designs, we have achieved integrated SFB device with an overall direct solar-to-output electricity efficiency (SOEE) of 14%. We have further improved the cycling performance of the SFBs by integrating robust organic redox couples. To enable SFBs in practical distributed and standalone solar energy conversion and storage systems in remote locations, we aim to keep a low overall cost for SFB devices while maintaining its high performance, thus lowering the chemical cost of redox active materials could be one of the effective ways to achieve such goal. Therefore, we are particularly interested in new, inexpensive, and robust redox couples with diverse redox potentials.


Wenda Wu, Jian Luo, Bo Hu, Camden Debruler, Maowei Hu and Tianbiao L. Liu; Department of Chemistry and Biochemistry, Utah State University, Logan, Utah, United States.

During the last decades, the demand for environmentally friendly renewable power source has grown rapidly to achieve the sustainable society. To efficiently utilize the widespread but intermittent renewable energy source such as solar and wind energy, low-cost and reliable large-scale energy storage technologies were required. Aqueous organic redox flow batteries (AORFBs) with the merits of decoupled energy and power, higher current and high power performance, safety features, synthetic tunability of charge storage molecules, and potentially low-cost, are ideal solution for the intermittent energy storage and electricity grids balancing. Herein, we designed and synthesized sulfonate functionalized viologen compound [1,1'-bis(3-sulfonatopropyl)-4,4'-bipyridinium], (SPr)$_2$V as a low-cost, highly soluble anode material for pH neutral AORFB application. DFT computational studies suggested charge repulsion and size exclusion enable the compatibility of (SPr)$_2$V with a cation exchange membrane. The superior chemical stability of the (SPr)$_2$V anolyte was confirmed by a 0.5 M half-cell (SPr)$_2$V/Br$_2$ battery test. Paired with the inexpensive I$_2$/catatholyte, the (SPr)$_2$V/I neutral AORFB delivered 1.0 V battery voltage and up to 71% energy efficiency with 99.99% capacity retention per cycle. When combined with (NH$_4$)$_2$Fe(CN)$_6$, a 0.9 M or 24.1 Wh/L symmetric (SPr)$_2$V/(NH$_4$)$_2$Fe(CN)$_6$ delivered ultra-stable cycling performance, nearly no capacity decay for 1000 cycles. To further boost the battery voltage and energy density of the (SPr)$_2$V-based AORFBs, Br$_2$/Br catholyte was chosen to combine with (SPr)$_2$V for AORFB demonstration. The (SPr)$_2$V/Br AORFB delivered 1.51 V battery voltage and 30.4 Wh/L operated energy density due to the high potential of Br$_2$/Br redox couple and high solubility of (SPr)$_2$V anode material. Furthermore, the (SPr)$_2$V/Br AORFB maintained excellent energy and power performance under 1.5 M concentration, respectively, up to 78% energy efficiency and 228 mWh/cm$^2$ power density, which is the highest power density ever reported in neutral AORFBs.

Ref:
Highly soluble redox-active polymers (RAPs) and colloids (RACs) \cite{1} are a new class of materials in the form of fluid dispersions that support a new concept in size-exclusion flow batteries. Because RAPs and RACs rely on intra-particle charge transfer to yield quantitative charge accessibility and high rate, understanding the intrinsic properties of these particles, as opposed to them in the bulk fluids, is of great interest to understand their limitations and to identify design opportunities. In this talk, I will present on the use of RAPs and RACs through a spectrum of powerful electrochemical techniques, ranging from spectroelectrochemical approaches to single-particle analysis.

In a first application, I will describe how nano-resolved scanning electrochemical microscopy (SECM) and its combination with Raman spectroscopy has helped us understand the mechanisms of individual electrochemical entities. These experiments provide us with unprecedented versatility to identify kinetic bottlenecks, such as charge trapping, and to determine the maximum current densities attainable in flow devices. Our data indicate that RACs undergo some conditioning upon electrolysis, and that their charge transport is sensitive to state-of-charge (SoC).

In a second application, I will describe how new redox mediation electrocatalysis using each redox-active pendant in RAPs as an electron transfer agent can be exploited to solve pervasive problems with passivating interfaces in complex chemistries, such as those involved in Li-air batteries. Here, investigations of charge transfer and of transient titration of reaction intermediates allow us to understand electrocatalysis, and the conditions that lead to effective storage or to failure. We expect that our methods will be extendable to other energy storage systems of interest to the community.

**References**


Diffusion-Free Grotthuss Topochemistry for High-rate and Long-Life Proton Batteries

Redox flow batteries (RFBs) are some of the most promising energy storage systems because of their scalability and design flexibility; however, their low energy density is a major drawback limiting their widespread application. Most conventional approaches to increase the energy density have involved exploiting high-concentration electrolytes. However, this approach results in many technical issues such as increased viscosity and sluggish kinetics. In this work, we propose a strategy of boosting the energy density by exploiting an active material based on phenazine molecule (5,10-dihydro-5,10-dimethyl phenazine or DMPZ), which is capable of multi-redox reaction at ~0.15 and 0.61 V vs Ag/AgCl. This novel positive electrode material exhibits reversible double-redox activity with fast kinetics and remarkable chemical stability. Coupled with 9-fluorone (FL), the DMPZ/FL flow cell can provide the highest energy density per mole (=85 Wh kg$^{-1}$) ever reported for RFBs. Furthermore, the marked color change of DMPZ at different charged states enables the state of charge to be precisely visualized. This novel strategy on multi-electron redox material can provide a potential pathway toward high-energy-density RFBs.

11:15 AM ES01.03.06
Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Intermittent sunlight necessitates the storage of electricity, ideally in controlled chemical reactions analogous to photosynthesis. Many efforts have focused on the oxidation of water at metal oxide semiconductor surfaces, although light-driven electrochemical reactions at photoelectrodes continue to suffer from sluggish half-reactions. One major challenge continues to be the control of multi-electron transfer events with well-defined rate constants. An ideal materials design approach would enable predictable rate constants prior to photo-electrode fabrication.

Electrodes comprised of organic semiconductor films offer the possibility to control redox processes independent of opto-electronic behaviors, making these electrodes a new idea for next-generation photoelectrodes. Examples of proof-of-concept include photo-capacitors and photo-driven water splitting. Yet to date, electron-transfer rates between conductive polymers and redox species remain slower than inorganic materials including metals and oxides, making it difficult to incorporate these inexpensive, printable systems in redox flow systems.

Most recently, we showed that the rate of electron transfer is predictable using a Marcus-Gierischer relationship, whereby the dominant factor controlling the rate of electron-transfer is the overlap in the density of states of the electrode with the density of states of the redox probe. With this new insight, we demonstrated that the microstructure of the polymer electrode becomes a critical component to controlling the symmetry of charge transfer reactions. Control of the microstructure enables moving the charge transfer events into the mass transport limit necessary for energy storage systems.

In this work, we focus on nanoscale manipulation of electron transfer events, relative to mass transfer of the redox probe, to further control electrode performance. Specifically, we investigate the role of heterogeneity of blended polymer electrodes. Both macroscale and nanoscale electrochemical phenomena will be discussed using a combination of spectroelectrochemical and scanning electrochemical microscopy. We demonstrate that the macroscale rate of electron transfer can be further controlled beyond the density of states framework, offering a new paradigm to control multi-electron transfer events not available in inorganic systems.

SESSION ES01.04: Redox Organic Electrode Materials in Metal Ion Batteries I
Session Chairs: Philippe Poizot and Hui Zhan
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 126 A

1:30 PM *ES01.04.01
Some New Considerations on Aqueous Rechargeable Batteries
Xiulei (David) Ji$^{1,2}$, Jun Lu$^2$ and Alex Greaney$^3$; Department of Chemistry, Oregon State University, Corvallis, Oregon, United States; $^1$Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois, United States; $^2$Materials Science and Engineering Program, University of California, Riverside, Riverside, California, United States.

There is a pressing need for new battery technologies in two key areas: high-energy power batteries for electric vehicles, and large-scale storage batteries to buffer the output from the renewable-but-intermittent solar and wind power generation. For storage batteries, the goal is to minimize the levelized energy cost over the devices’ lifetime. This means that electrode materials containing rare and expensive elements should be avoided. Secondly, the cycle life of storage batteries must be excellent — ideally over 10,000 cycles. Thirdly, these batteries should be quickly rechargeable to store, for example, energy from wind farms. Most importantly, storage batteries should be intrinsically safe, i.e., nonflammable. To meet this list of requirements, batteries with aqueous electrolytes exhibit several distinct advantages. Aqueous electrolytes are cheaper and safer. The simplicity of an aqueous chemistry environment may facilitate long battery longevity, and its high conductivity brings an innate power advantage. In battery chemistry design, one of the most important considerations is the choice of working charge carriers. To date, a major portion of battery technologies rely on metal-ion charge carriers. Surprisingly, non-metal cations, particularly proton-containing cations, i.e., $^1\text{H}^+$, $^2\text{H}^+$ and $^3\text{H}^+$, have received exceedingly little attention. The simplest form of hydrogen cation, a single proton, is nearly “invisible” with a measured radius of ~0.89 fm or ~2.1 fm, using muon or $^3\text{He}$ spectroscopy, respectively. Due to the negligible strain of hosting protons, the rate capability and cycle life of proton batteries have the potential to be far superior to those of existing batteries. In this talk, I will introduce some of our new results, experimental and computational, on the storage of new charge carriers in battery chemistry for grid-storage purposes, particularly related to the Grotthuss mechanism and the ion/electrode interactions. I will compare different charge carriers in terms of their correlations to electrochemical properties, such as capacity fading, polarization, and operation potentials.

References

2:00 PM ES01.04.02
Development of Organic Electrode Materials for Anion-Ion Batteries
Thibaut Gutel$^1$, Vincent Cadieu$^2$, Léon Merchat$^3$, Jeremie Salomons$^4$, Lionel Dubois$^4$, Dominique Guyomard$^1$ and Philippe Poizot$^2$; CEA, Grenoble, France; $^1$Université Grenoble Alpes, Grenoble, France; $^2$Institut des Matériaux Jean Rouxel, Nantes, France. Nowadays electrodes of lithium batteries are mainly constituted by inorganic compounds based on transition metals such as cobalt, nickel or manganese. Although their performances are satisfying, these materials present several important drawbacks. Indeed these compounds are expensive because they are prepared due to energy-consuming techniques from rare mineral precursors. Moreover, some metals are toxic and often hard to recycle. Eventually their reactivity leads to safety issues in abusive conditions. Organic electroactive compounds such as nitroxide based polymers or carbonate salts offer a cost-effective and environmental friendly alternative to conventional electrode materials for electrochemical storage. Interestingly these products can be prepared from low cost precursors using classical organic and polymer chemistry techniques. Moreover these compounds are easy to recycle or reuse at their end of life. Eventually organic electrode materials can followed n-doped but also p-doped redox mechanisms which enable to
imagine new battery configurations (cation-ion, dual-ion or anion-ion). But until now, their use is still challenging due to low cycle life usually related to their high solubility in organic solvents of electrolytes. Following the pioneer work of Yao et al. with its concept of molecular-ion based “rocking chair” battery, this work is focused on the development of optimized full organic battery using anion as a shuttle during charge/discharge in order to study their electrochemical performances for in particular high power applications.

First various polymers based on viologen redox unit were studied as negative electrode materials and the introduction of crosslinker but also the influence of the nature of counter-anion have been investigated. A particular strategy was identified in order to stabilize the specific capacity of polyviologen (PV) along cycling. In parallel, an original and insoluble structure based on lithium diaminoterephthalate (Li2DAnT) has been developed and even if some moderate electrochemical performances have been obtained, this development depends strongly for the first time the interest of terephthalate backbone to suppress the dissolution of p-doped organic materials. Finally the formulation of organic electrodes using PV, Li2DAnT but also using polynitrooxides (PTMA+) based composites were optimized in particular for screen printing process and several full organic batteries have been assembled and tested in anion-ion configuration. These results pave the way for the development of metal-free battery with high electrochemical performances.

4 M. Yao et al., Sci. Reports, 2015, 5, 10962-10969;10962
5 Sano et al., Appl. Materials & Interfaces, 2013, 5, 1355-1361

2:15 PM ES01.04.03
Forming Stable Cathode-Solid Electrolyte Interface—Benefits of Organic Electrode Materials in All-Solid-State Batteries Fang Hao1, Xiaoweil Chi1, Yanliang Liang1, Rong Xu2, Hua Guo3, Kjeji Zhao4, Jun Lou4 and Yan Yao1; 1University of Houston, Houston, Texas, United States; 2Purdue University, West Lafayette, Indiana, United States; 3Rice University, Houston, Texas, United States.

Forming stable cathode-solid electrolyte interface is one of the greatest challenges in sulfide-based all-solid-state sodium batteries (ASSSBs). So far these ASSSBs suffer from low specific energy and poor cycling performances due to the interfacial incompatibility between cathode materials and sulfide electrolytes. Resistive layer forms at the interface due to the electrolyte decomposition at high potentials. Most previous cathodes are also too rigid to accommodate the volume change upon cycling, resulting in the inter-particulate contact loss. Herein we show an organic cathode material, pyrene-4,5,9,10-tetrone (PTO), that can form an (electro)chemically and mechanically compatible interface with Na2PS4. PTO has a moderate redox potential (2.2 V vs. Na+/Na) that aligns with the electrochemical stability window of Na2PS4. PTO also has a low Young’s modulus (4.2 × 0.2 GPa) that is similar to that of Na2PS4 (10.7 × 0.6 GPa), hence ensuring intimate PTO-Na2PS4 contact during cycling. The PTO-based ASSSB exhibits high specific energy of 587 Wh kg-1 at material-level and 89% capacity retention over 500 cycles. This work reveals an effective cathode design strategy towards compatibility with solid electrolytes and thus high-performance ASSSBs.

2:30 PM ES01.04.05
Redox Polymers with Heteroaromatic as Electrode-Active Materials for Batteries Birgit Esser1; 2; Institute for Organic Chemistry, University of Freiburg, Freiburg, Germany; 2Freiburg Materials Research Center, University of Freiburg, Freiburg, Germany.

In face of the climate change there is a strong and growing demand for the storage of renewable energies. Organic electrode materials have attracted great interest, as they can be prepared from renewable, sustainable or limited-resources, they are easy to recycle as well as potentially safer and cheaper to produce, leading to a low carbon footprint. A promising class of organic electrode materials are redox polymers — polymers containing groups that can be reversibly reduced or oxidized. In this talk organic redox polymers will be presented containing heteroaromatics as redox-active functionalities. The design, synthesis and electrochemical properties of these polymers will be discussed as well as their application as electrode-active materials in batteries. Mechanistic studies will be presented that show how the mobility of the redox polymer within the composite electrode as well as interactions between redox-active groups influence the specific capacity of the electrode as well as its cyclability.

4:00 PM ES01.04.05
Structure, Function and Electrochemistry of Novel Hybrid Organic/Inorganic MOFs Energy Storage Materials Kevin V. Nielson, Yujing Bi, Liping Zhang and Tianbiao L. Liu; Utah State University, Logan, Utah, United States.

The structure tunability and built-in porosity of metal organic frameworks (MOFs) materials makes them promising electrode materials to host metal ions. Herein, Novel MOFs materials consisting of redox active ligands and earth abundant transition metals were rationally designed and synthesized for ion intercalation energy storage applications. Structural characterization by X-ray diffraction, IR absorption, and elemental analysis confirmed target structures were assembled successfully. Electrochemical studies including cyclic voltammetry, electrochemical impedance spectroscopy, and full cell battery tests were conducted to verify these organic/inorganic materials have improved electrochemical reversibility, conductivity, and stability over purely organic or inorganic materials. For example, a Ni redox MOFs delivered outstanding battery performance for 1000 cycles with capacity retention up to 82%. Further studies on ionic conductivity, valence state analysis, gas adsorption, and charge storage mechanism were conducted to better understand the electrochemistry, structure/function relationship of these novel MOFs materials.

4:15 PM ES01.04.06
High Capacity and Long Cycle-Life Quinone-Type Active Materials for Use in Rechargeable Batteries Maseun Yao, Hisanori Ando, Tetsu Kiyobayashi and Nobuhiko Takeichi; AIST (National Institute of Advanced Industrial Science and Technology), Ibeda, Japan.

Using a redox active organic material as an electrode material of rechargeable lithium batteries can reduce the amount of minor metal-based materials from the current system. Among many organic candidates, we have focused on a series of low-molecular-weight quinone derivatives since they show high capacities based on their multi-electron transfer type redox reaction. However, many of them often show poor cycle-stabilities; therefore, improving the cycle-stability is an important concern. One of the reasons for the capacity fade is believed to be the dissolution of redox-active low-molecular-weight molecules into the electrolyte solution.

To suppress the solubility of the quinone-based molecules, we synthesized some oligomers in which the quinone sites are connected by some covalent bond or fused, and proved that these oligomers have longer cycle-lives than the monomers. For example, anthraquinone (AQ), a quinone containing the anthracene skeleton, shows a high initial discharge capacity of about 200 mAh/g with the average potential of 2.3 V vs. Li+/Li; however, its capacity notably decreases upon cycling. On the other hand, a fused larger polycyclic quinone having the pentacene skeleton (pentacenetetrone), which has lower solubility, exhibits a longer cycle-life than AQ. In addition, the solubility of the AQ derivatives can be lowered by oligomerization. We synthesized an AQ dimer and trimer, in which the AQ units are connected by the acetylene unit, and found that they are insoluble in ordinary solvents and show a longer cycle-performance. In particular, the trimer retained an almost constant capacity during the one hundred cycles. A similar result was also observed for the naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) derivatives which undergo a four-electron transfer redox reaction. While the lithium salt of the naphthazarin itself (monomer) showed a high capacity of about 400 mAh/g with the average potential of 2.7 V vs. Li+/Li during the first cycle, its cycle stability was also poor. On the other hand, a dimer fused by the dithiin ring showed an improved battery performance; a high initial capacity of 416 mAh/g with a relatively stable cycle-performance was obtained.

We consider that the above-mentioned oligomers have a stronger attractive intermolecular force than the monomers which should contribute to a less solubility than the monomers. To obtain a theoretical insight into the intermolecular interactions, a quantum chemistry calculation was performed. Our calculation gave x-stacked structures for a series of the AQ oligomers, the charged naphthazarin and its fused dimer. The estimated binding energy for the monomers are about 20 kJ/mol, which are typical values for such stacked small molecules. As for the oligomers, a few times higher values (70-100 kJ/mol) were obtained. In general, intermolecular forces represented by the Van der Waals forces are considered to be very weak; however, the obtained stacking force values are much higher than the binding energy of the hydrogen bonding (10-40 kJ/mol) which is a relatively strong intermolecular force and comparable to the level of the covalent bonding (100-300 kJ/mol). This calculation indicates that oligomerization will be very effective to enhance
the intermolecular attractive interaction which should contribute to suppressing the dissolution. In summary, the oligomerization and/or ring-fusion of a redox active molecule showing multi-electron transfer reaction will be a guide for designing a new organic active material that can satisfy both the long cycle-life and high energy density requirements.

4:45 PM ES01.04.07
Molecular Design Strategies to Achieve Multi-Electron Redox Reactions of N-Containing Heterocyclic Molecules for High Voltage and Energy Electrode Materials
Ji Eon Kwong, Dong Joo Min, Kyu Nam Lee and Soo Young Park; Seoul National University, Seoul, Korea (the Republic of).

Organic redox-active molecules composed of only earth-abundant elements such as C, H, N, O, and S are very promising for the next-generation secondary batteries with low cost and sustainability. A lot of organic cathode materials have been reported, so far; however, their redox potentials are still mostly below 3.0 V vs. Li/Li⁺ which is considerably inferior to the conventional ones. Recently, a few organic molecules showing redox potential above 3.5 V vs. Li/Li⁺ are reported including triphenylamine (TPA), carbazole (Cbz), and phenothiazine (PTZ), whose charge/discharge mechanisms rely on oxidation reactions of N-containing heterocyclic redox centers. Although they show excellent cycle stability and high rate performance, most of them can undergo only a one-electron oxidation reaction, which limits their practical capacity below 100 mAh/g. Here, we report molecular design strategies to achieve a large specific capacity of the N-containing heterocyclic organic molecules by inducing multi-electron redox reactions. First, a series of novel organic molecules bearing phenoxazine (PXZ) as a new p-type redox center is reported. In the molecules, multiple PXZ units are covalently connected together by a phenyl ring core as a minimal linker. Through the combination of experimental and theoretical studies, it is revealed that the three-dimensional molecular geometry and the negligible re-organization during the redox reactions allow them to undergo reversible multi-electron redox reactions with minimal redox peak splitting. In the coin cells, they can deliver large specific capacity of more than 120 mAh/g with a discharge plate at 3.7 V vs. Li/Li⁺. It is noteworthy that they show excellent cycle stability over 500 cycles and good rate capability.

Second, we present a series of fixed pyrroles recently developed in my group as a new cathode active materials. They exhibit multi-electron oxidation reactions at above 3.5 V vs. Li/Li⁺ to provide large specific capacity. Their electrochemical properties and electrode performances are discussed in this presentation.

SESSION ES01.05: Poster Session: Organic Materials for Energy Storage
Session Chairs: Tianbiao Liu and Philippe Poizot
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES01.05.01
Viologen Redox Flow Batteries for Scalable and Sustainable Energy Storage
Bo Hu and Tianbiao L. Liu; Chemistry and Biochemistry, Utah State University, Logan, Utah, United States.

Redox flow batteries (RFBs) are a viable technology to store renewable energy in the form of electricity that can be supplied to electricity grids. However, widespread implementation of traditional aqueous inorganic redox flow batteries (AIRFBs), such as vanadium and Zn-Br, RFBs, is limited due to a number of challenges related to materials, including low abundance and high costs of redox-active metals, expensive separators, and corrosive and hazardous electrolytes. To address these challenges, our group has demonstrated a series of pH neutral aqueous organic redox flow batteries (AORFBs) based on tunable and sustainable viologen anolytes (e.g. methyl viologen (MV), 1,1′-bis[(3-trimethylammonio)propyl]-4,4′-bipyridinium ([NPr]2MV), and 1,1′-bis[3-sulfonatopropyl]-4,4′-bipyridinium ([SPr]2MV) with a variety of organic and inorganic catholytes. Viologen compounds display excellent chemical and electrochemical stability, desirable redox potential, and high solubility in water. The MV/FcNCI (FcNCI abbreviated for ferrocenyl(methyl)trimethylammonium chloride) AORFB was reported by us with outstanding cycling stability and power density, representing as a benchmark organic flow battery. By means of molecular engineering, we have not only tuned the molecular structures of viologen molecules and also achieved even better stability compared to the benchmark molecule, methyl viologen. These efforts have led to several outstanding pH neutral AORFBs: (1) the ([NPr]2V)/FcNCI anolyte, achieving a cell voltage of 1.72 V and a power density of 130 mW/cm²; (2) The 1.38 V ([NPr]2V)/TEAPORFB represents the most stable total organic RFB (99.93% capacity retention per cycle for overall 500 cycles), and (3) the ([SPr]2V/(NH4)2Fe(CN)6 AORFB represents the most stable AORFB (nearly 100% capacity retention after 1000 cycles) with a demonstrated high capacity (24.1 Ah/L). The presented high performance viologen AORFBs underline the great promise of scalable redox-active molecules for green energy storage. Particularly, this poster presentation emphasizes that fundamental understandings of redox-active electrolytes at molecular level are crucial to develop new generations of redox flow batteries for large scale and dispatchable renewable energy storage.

References:
(10) Filed US Patents covering applications of water soluble viologen, ferrocene derivatives, and TEMPO for RFBs.

ES01.05.02
Supercapacitors from Solution-Processed Composites
Nelson E. Coates, John Wang and Jeffrey Urban; Lawrence Berkeley National Lab, Berkeley, California, United States; California State University - Maritime Academy, Vallejo, California, United States.

To accelerate the deployment of non-fossil fuel based transportation and grid-scale energy generation technologies, both high-power, and high-energy storage devices are needed. Supercapacitors are an emerging technology that can meet both of these storage needs by combining the high energy densities traditionally associated with batteries, with the high power densities traditionally associated with capacitors. Here, we describe recent progress fabricating capacitors from solution-processed composite materials, which is promising way to achieve high-performance supercapacitor architectures from a wide variety of electrode materials.

In their most simple form, capacitors can be thought of as geometric devices consisting of two conductors separated by an insulator. These two conductors can hold opposite charges, and thus store energy by creating an electric field in the volume of space between the two conductors. Because capacitors can store energy merely by moving charges in conductors as opposed to relying on slower electrochemical reactions to create mobile charges, they naturally have the ability to source higher power than batteries. But because simple capacitors do not store any energy in chemical reactions, they suffer from lower energy storage capacities than batteries. The amount of energy that is able to be stored in capacitors is much smaller than their curvature or area. Existing research into increasing the areas of capacitor electrodes, and decreasing the separation distance between them has been limited by the number of available electrode materials that can form structures with a continuous network of interpenetrating electrode phases, while still preventing charge transfer or electrochemical reactions between the electrodes.

A promising way to engineer a material geometry combining conducting phases with an enormous interfacial area separated by a very thin insulating layer is by using solution-cast materials. Solution-processing permits the mixing of a wide range of morphologically and chemically distinct electronic materials, which can either undergo non-equilibrium phase separation or spinodal decomposition into composites that have an enormous interfacial area to volume ratio and extremely small separation between the two phases. Our
preliminary results demonstrate that solution-processed composites have great potential for achieving high-performance capacitor architectures with a wide variety of electrode materials.

ES01.05.03

Organosilyl Nitrile and Organosilyl Nitrile/Carbonate Blend Electrolytes for Lithium-Ion Battery Applications Leslie J. Lyons1, Scott Beecher2, Evan Cunningham1, Tom Derrah1, Steven Sharp1, Shengyi Su1, Seiyong Yoon1, Junmin Zhu1, Monica Usrey2, Adrian Peña-Hueso3, Tobias Johnson4 and Robert West5; 1Department of Chemistry, Grinnell College, Grinnell, Iowa, United States; 2Silatronix, Inc., Madison, Wisconsin, United States.

Novel organosilicon nitrile (OSN) solvents have low flammability, broad electrochemical windows and excellent thermal stability, which make them promising materials for lithium-ion battery (LIB) electrolytes.1 This presentation will explore the ion transport of a variety of electrolytes composed of the organosilyl nitrile (OSN) solvents which vary in the degree of carbonation ions. The nonaqueous electrolyte media are also essential to offer wide electrochemical windows which have been studied for the role of posolys in nonaqueous medium while only a few nitrile electrolytes have been designed in this system.2 Herein, we present a new category of fused heterocyclic rings that can be employed as the negolyte. Our attempts to introduce various substituents to the core cyclic ring altered the electrochemical and chemical reversibility.

Redox flow batteries (RFBs) are one of the promising energy storages with a grid scale owing to their decoupled energy and power density, which lead to scalability and flexibility in design. To aim at higher energy density more than that of the current technology of vanadium RFBs, the redox-active molecules should have higher solubility and larger voltage gap than vanadium. The nonaqueous electrolyte media are also essential to offer wide electrochemical windows for RFBs. Many redox-active organic materials have been studied for the role of posolys in nonaqueous medium while only a few nitrile electrolytes have been designed in this system.2 Herein, we present a new category of fused heterocyclic rings that can be employed as the negolyte. Our attempts to introduce various substituents to the core cyclic ring altered the electrochemical and chemical reversibility.

The degree of molecular planarity and Lewis acidity/basicty of redox-active heterocyclic molecules critically determine the reversibility in cyclic voltammetry profile. The decorations of functionality also shift the redox potential and the number of electrons transferred. In addition, the asymmetric structure of heterocyclic rings may increase the solubility in the nonaqueous media. Through the fundamental studies on the design of heterocyclic rings and the corresponding electrochemical/chemical analyses, we demonstrated the optimum negolyte that can potentially provide high energy density and cyclic stability in nonaqueous RFBs. This study gives the guideline to develop new redox-active organic molecules for the application of RFBs.

References

ES01.05.04

A New Class of Redox-Active Heterocyclic Rings Applied for Negolytes in Nonaqueous Redox Flow Batteries Seun Kim1, Jin Hyek Jung2, Junmin Joo1 and Hye Ryung Byon1,2; 1Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of), 2Advanced Battery Center, KAIST Institute for NanoCentury, Daejeon, Korea (the Republic of). Herein, we present a new category of fused heterocyclic rings that can be employed as the negolyte. Our attempts to introduce various substituents to the core cyclic ring altered the electrochemical and chemical reversibility.

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References
Mellitic Trimides Showing Three One-Electron Redox Reactions for Large Capacity Organic Electrode Materials Dong Joo Min, Ji Eon Kwon and Soo Young Park; Seoul National University, Seoul, Alabama, United States.

Since the development of the transition metal oxide-based electrodes has been reaching its theoretical limits, organic electrode materials have attracted much attention as alternatives due to light weight, abundance, low cost, sustainability, and chemical diversity. Among others, cyclic imides, which consist of two acyl groups bound to a nitrogen atom, are one of the most promising redox centers for organic electrode materials due to their stable and reversible one-electron reduction. Although a lot of organic electrode materials bearing two cyclic aromatic imides such as perylene diimides, naphthalene diimides, and pyromellitic diimides showed superior cycle and rate performance, they can deliver rather low specific capacities. In fact, regarding their reversible two-electron reduction, the theoretical capacities of the diimide cores possessing no substituents at the two N-positions are up to 137, 201, 248 mAh/g for perylene, naphthalene, and pyromellitic diimide, respectively. Practically, small substituents are necessarily required to utilize them for electrode materials, which typically limits their practical capacity far below 200 mAh/g.

Here, we present a series of mellitic trimides which bear three cyclic imide groups fused to one phenyl ring with C3-symmetry. Theoretically, the non-substituted mellitic trimide core is able to accept three electrons to deliver a specific capacity up to 282 mAh/g. As a model compound, ethyl-substituted mellitic trimide (ETI, theoretical specific capacity = 218 mAh/g) shows well distinguished and reversible three-onelectron redox reactions at -0.97, -1.62, and -2.36 V vs. Ag/Ag+, respectively, in the cyclic voltammetry experiments. In the galvanostatic charge/discharge test, ETI electrode delivers a specific capacity of 225 mAh/g, one of the highest capacity among the imides electrodes, with three distinct plateaus at 2.82, 2.30, and 2.09 V vs. Li/Li+, respectively, in the coin cell.

Organic Semiconductor (Photo)electrodes in Redox-Based Electrochemical Flow Cells Zhiting Chen, Jonathan Harris, Bharati Neelamraju, Melanie Rudolph and Erin L. Ratcliff; The University of Arizona, Tucson, Arizona, United States.

Controlling interfacial electron-transfer rates is fundamental to maximizing device efficiencies in electrochemical technologies including redox-flow batteries, chemical sensors, bioelectronics, and photo-electrochemical devices. In many of these technologies, control of multi-electron transfer events with well-defined rates constants is required, but is often limited by natural choices. Electrodes comprised of organic semiconductor films offer the possibility to control redox properties independently of opto-electronic behaviors, making these electrodes idea for next-generation photoelectrodes. Yet to date, electron-transfer rates between conductive polymers and redox species remain slower than inorganic materials including metals and oxides. Most recently, we showed that the rate of electron transfer is predictable using a Marcus-Gerischer relationship, whereby the dominant factor controlling the rate of electron-transfer is the overlap in the density of states of the electrode with the density of states of the redox probe. With this new insight, we demonstrated that the microstructure of the polymer electrode becomes a critical component to controlling the symmetry of charge transfer reactions. In this work, we focus on nanoscale manipulation of electron transfer events, relative to mass transfer of the redox probe, to further control electrode performance. Specifically, we investigate the role of heterogeneity of conductive polymer electrodes, using a model system comprised of varying sized ultra-microelectrodes formed from blends of poly(3-hexylthiophene) (P3HT) and poly(methyl methacrylate) (PMMA). We demonstrate that the mcraque rate of electron transfer can be further controlled beyond the density of states framework, offering a new paradigm to control multi-electron transfer events.

An Analysis of Lithium Sulfur Interactions via GITT Measurements Daisy Patino, Bo Dong, Ruoxu Shang, Taner Zerrin and Cengiz S. Ozkan; University of California, Riverside, Riverside, California, United States.

The galvanostatic intermittent titration technique (GITT) is an electroanalytical tool commonly used in lithium ion technologies which uses transient and steady state measurements to obtain kinetic and thermodynamic properties of electrodes materials. The GITT procedure involves applying short current pulses followed by relaxation periods. In conventional lithium ion cells, when we apply current pulses, we induce concentration changes within the host electrodes. In lithium sulfur batteries however, the concentration change occurs in the electrolyte due to the reduction process of sulfur to electrolyte-soluble polysulfides. Hence, it is a complex procedure to quantify values such as, chemical diffusivity coefficient of lithium ions and the resistivity through the electrolyte in lithium sulfur cells, as opposed to conventional solid state lithium ion cells. Accordingly, research efforts to utilize GITT for lithium sulfur cells, omit the polysulfide shuttle mechanism to obtain a semi-solid state model. Herein, we explore a complete lithium sulfur model that enables more accurate qualitative depictions for mass transport rates, chemical reaction rates, and sulfur utilization.

Improved Radical Stability of Violanolytes in Aqueous Organic Redox Flow Batteries Maowei Hu, Bo Hu and Tianbiao L. Liu; Chemistry and Biochemistry, Utah State University, Logan, Utah, United States.

Redox flow batteries (RFBs) are a viable technology to store renewable energy in the form of electricity that can be supplied to electricity grids. Methyl viologens are a highly attractive anode material due to it high solubility in water, low cost, fast electrochemical kinetics, and excellent chemical stability under pH neutral conditions. Our group reported a 1.2 V methyl viologen (MV)/4-hydroxyl-TEMPO (4-HO-TEMPO) neutral aqueous organic redox flow battery (AORFB) and a high theoretical energy density FeNCU/MV AORFB. In this presentation, we introduce a highly stable 1.38 V viologen/TEMPO AORFB using 1,1'-bis[3-(trimethylammonio)-propyl]-4,4'-bipyridinium tetrachloride known to date. Compared to the (NPr)2-TEMPO as a catholyte. The (NPr)2-V/NMe4-TEMPO AORFB displayed outstanding cycling stability, 97.48% total capacity retention or 99.995% capacity retention per cycle for 500 cycles at 60mA/cm2 and a high power density of 128.2 mW/cm2 under pH neutral conditions, representing the most stable total AORFBs known to date. Compared to the (NPr)2-V/NMe4-TEMPO AORFB (97.48% total capacity or 99.995% capacity retention per cycle), the long-term cycling stability of the MV/NMe4- TEMPO AORFB (91.21% total capacity, which is equivalent to 99.982% capacity retention per cycle) is apparently inferior to that of the (NPr)2-V/NMe4-TEMPO. We believe that the more stable charged state, [(NPr)2V]+, than [MV]+ contribute to the observed improved cycling stability of the (NPr)2-V/NMe4-TEMPO AORFB. To confirm this hypothesis, we used UV-vis absorption spectroscopy test the radical stability of [(NPr)2V]+ and [MV]+ (0.1 mM in 2 M NaCl). Over 48 hour continuous measurements, the absorption of [MV]+ showed a slow decay. For [(NPr)2V]+, almost no absorption decrease was observed. This studies confirmed that the outstanding cycling stability of the (NPr)2-V/NMe4- TEMPO AORFB is attributed to the exceptional radical stability of [(NPr)2V]+. The present study not only stresses the importance of the molecular engineering strategy to improve active materials’ stability but also advances the state of the art AORFBs for sustainable and green energy storage of renewable energy. Reference


SESSION ES01.06: Redox Organic Electrode Materials in Metal Ion Batteries II
Session Chairs: Stéven Renault and Yan Yao
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 126 A

8:00 AM ES01.06.01
PTMA@CTAB Core-Sphere Nanospheres Hybrids with Reduced Graphene Oxide as High-Performance Free-Standing Cathodes For Lithium-Ion Batteries He Jia and Jean-Francois Gothy; Institute of Condensed Matter and Nanosciences, Division of Bio and Soft Matter, Université catholique de Louvain, Louvain-la-Neuve, Belgium.

High-performance lithium-ion batteries based on organic active materials currently constitute one of the most investigated energy sources due to their inherent advantages such as renewability, lightness, fast charge and discharge, and more environmentally friendly features. Among different active organic materials investigated so far, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA), a polymer bearing persistent nitroxide radicals as repeating units, has become one of the most promising candidate as cathode polymeric material for lithium-ion batteries, which exhibits fast reversible redox reactions and allows high energy storage, high potentials and a long cycling...
life. However, PTMA is easily dissolved into organic electrolytes and displays limited electrical conductivity, greatly hindering the performances of lithium ion batteries based on this polymer. Moreover a high mass loading of PTMA leads to the aggregation of active materials which cannot be fully utilized and hence in a decrease of the lithium performance of the battery.

Here, we report a facile and novel method for the fabrication of high performance free-standing cathodes using PTMA/CTAB nanospheres as active units and rGO@MWCNT as conductive framework. The introduction of PTMA nanostructures and their uniform distribution in the composite system shortens the ionic pathways in the active material and allows almost 100% active substance utilization. At the same time, the GGO coating on each of PTMA nanosphere not only effectively increases its stability in the electrolyte (0.03% capacity loss per cycle), but also avoids the aggregation of PTMA and leads to a high effective mass loading of active material. Most importantly, the composite electrode shows as high as 105 mAh/g specific capacity based on the mass of the whole electrode in the voltage range from 2V to 4V, which is almost the highest reported value for PTMA cathode materials. The presented work successfully improves conductivity and stability of PTMA as cathode which can be also extended to various organic materials to obtain high performance free-standing electrodes.


8:15 AM ES01.06.02
Solution-Processable Electroactive Polymers as Active Materials for Macroscale Energy-Storage Devices with High-Rate Capability
Jeffrey W. Long1, Megan B. Sassin2, Ashley N. Hoffnester1, Anna Österholm1, Chin Lo3 and John Reynolds2
1 Naval Research Laboratory, Washington, District of Columbia, United States; 2 Georgia Institute of Technology, Atlanta, Georgia, United States.

Electroactive polymers exhibit desirable properties for electrochemical storage, but their broader implementation is limited by the conventional methods by which they are prepared. Electropolymerization routes produce high-quality films, yet with thickness typically <1 μm. Solution-phase synthesis yields larger quantities of material, but in precipitate form that can be difficult to process into high-performance electrodes. The Reynolds group at Georgia Tech has recently introduced a family of solution-processable electroactive polymers, where solubility characteristics are controlled by derivatizing ProDOT and EDOT with particular side chains [1,2]. The ability to dissolve/disperse such polymers at high concentrations (e.g., in polar organic solvents) facilitates their incorporation into macroskopically thick carbon nanotube/nanofiber papers that serve as a base electrode architecture for macroscale devices. By distributing the polymer as a thin coating on a 3D carbon-based current collector, the fast-switching characteristics inherent to these ProDOT and EDOT polymers is maintained, while the capacity per geometric footprint is amplified by factors of ten or greater compared to analogous planar thin films. The chemical properties of these polymers can be further tuned for reactivity in either aqueous or nonaqueous electrolytes, which expands the range of electrochemical device configurations that will benefit from these charge-storing materials. We perform electrochemical tests on polymer-modified carbon paper electrodes in three-electrode half-cells and two-terminal devices, assessing such critical performance metrics as rate-dependent capacitance/capacity, self-discharge, and cycle life.

Pushing Further the Superlativity of Dilithium Benzenedipropiolate—Towards Extreme Capacities for Organic Electrode Materials

Daniel Brandelli, Antonia Kotronia, Marc Deschanps, and Stéven Renaud

1, Institut des Matériaux Jean Rouxel (IMN) - Université de Nantes, Nantes, France; 2Department of Chemistry - Ångström Laboratory, Uppsala University, Uppsala, Sweden; 3Blue Solutions, Quimper, France.

Organic electrode materials (OEMs) for lithium-ion batteries (LIBs) constitute a very promising alternative to standard electrodes materials that are prepared from finite and non-renewable minerals resources, since they instead are being potentially environmentally friendly, cheap, and abundant if derived from biomass via eco-friendly processes. However, their commercial use is currently held back, primarily due to their poor energy density. High specific capacity OEMs are therefore of uttermost interest. During the last 5 years, OEMs with the ability of an unexpected reversible reduction of carbon-carbon double bonds have sporadically been reported [1]. As a consequence of this redox process – coined ‘superlativity’ – specific energies several times higher than commercial standards (graphite) and Li/C ratios of 1/1 have been reported.

In a previous work on the ‘superlativity’ of dilithium benzenedipropiolate [2], we reported that this material can reversibly reduce its unsaturated carbon-carbon bonds in addition to the expected reduction of its carbonyls, leading to a Li/C ratio of 1/1 and specific capacity as high as 1363 mAh g⁻¹; the highest ever reported for a lithium carbonylate. However, the stability of this redox behavior was poor and obvious capacity fading was observed after a few cycles. We here show that better capacity and stability can be achieved with appropriate electrode formulation and optimization of parameters such as calendaring or temperature/electrolyte match (liquid or industrial quality polymer electrolytes).


Nickel-Salen Type Polymer as Conducting Agent and Binder for Carbon-Free Cathodes in Lithium-Ion Batteries

Jung-Hyun Kim, O'Meara Cody, Irina Chepurnaya, Mikhail Karushev, Sayth Dhamasaena, Hanna Cho, Benjamin Yurkovich, and Sam Koigan; 1Mechanical and Aerospace Engineering, Center for Automotive Research, The Ohio State University, Columbus, Ohio, United States; 2Powermers Inc, Westerville, Ohio, United States.

Polymeric salen-type metal complexes, often denoted as poly[M(Schiff)₂] (M = transition metals), is one of promising electronically conducting polymers. Among the poly[M(Schiff)₂] family, poly[Ni(CH₃-Salen)₃] has been most intensively investigated due to its promising electrochemical properties for energy storage devices such as supercapacitor and lithium-ion (Li-ion) battery. The poly[Ni(CH₃-Salen)] have been proven to have similar performance to other conducting polymers in terms of conductivity, while their commercial use is currently held back, primarily due to their poor energy density. High specific capacity OEMs are therefore of uttermost interest. During the last 5 years, OEMs with the ability of an unexpected reversible reduction of carbon-carbon double bonds have sporadically been reported [1]. As a consequence of this redox process – coined ‘superlativity’ – specific energies several times higher than commercial standards (graphite) and Li/C ratios of 1/1 have been reported.


PVdF Based Binder for Gelled Electrodes Used in Hybrid Polymer Lithium Battery

Helene Renaud, Olivier Prat, Djamel Mourzagh, Jeremie Salomon, Gaelle Besnard, Julio Abusleme, Daniel Glossener, and Marc-David Branda; 1 Commissariat à l’énergie atomique et aux énergies alternatives, Grenoble, France; 2Solvay Speciality Polymers, Bollate, Italy; 3Advanced Innovation Office, Solvay SA, Brussel, Belgium; 4Solvay R&I, Aubervilliers, France.

One of the most ambitious challenges for the planet for the next few future years is to reverse the worldwide CO2-related global warming and decrease the pollution of large modern cities by the burning of fossil fuels. Accordingly, the full or partial replacement of inner combustion engines by electric motors and the use of alternative green energy sources, such as solar or wind or geothermal for powering the stationary applications appear as necessary to reach these objectives, in conditions that energy storage systems could ensure a clean regulation the energy production. Henceforth, batteries and more especially rechargeable lithium batteries really represent a viable energy storage technology for supplying low-emission plug-in hybrid electric vehicles (HEVs), even for emission-free pure electric vehicles (EVs) or for the integration of renewable intermittent energy sources. Indeed, lithium based batteries exhibit high specific energy (high voltage charged with high specific capacity), long cyclelife, high efficiency, high charge/discharge rate capability and low self-discharge. In addition, it is a versatile technology easily adaptable to the application by playing with the electrode materials and electrolyte composition.

However, most commercial batteries widely use liquid electrolyte composed of organic solvents containing salt and impregnating a separator. This implies to define inevitably
Diversity-Oriented Approaches to Tailoring Ion-Selective Polymer Membranes for Aqueous and Non-Aqueous Electrochemical Devices

Moreover, assembled with hybrid polymer membrane without any addition of complementary electrolyte, the gelled electrodes work successfully at various discharge rates, even at high rates and exhibit a very stable behavior with very long cyclife.

References


SESSION ES01.07: Membranes and Electrolytes for Rechargeable Batteries I

Session Chairs: Brett Helms and Guihua Yu
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 126 A

2:00 PM +ES01.07.01
Diversity-Oriented Approaches to Tailoring Ion-Selective Polymer Membranes for Aqueous and Non-Aqueous Electrochemical Devices

Brett Helms, Lawrence Berkeley National Lab, Berkeley, California, United States.

Low-Cost and ion-selective membranes are required to meet the growing demands for peak performance by next-generation batteries for EVs, aviation, and the grid. To that end, I will showcase a highly disruptive membrane platform based on polymers of intrinsic microporosity, whose pores are on the length scale of solvated ions and small molecules that are sometimes used as the battery’s active materials (e.g., as in flow batteries). The design space for these polymer membranes is advanced using a variety of computational tools, including computational materials genomics. The foundational knowledge built using these tools provides a roadmap for the diversity-oriented synthetic development of polymer membranes with specific pore architectures and chemistry, specifically tailored for the battery’s chemistry. I will also outline foundations on which to build adaptive membranes, where judiciously placed molecular switches allow for the membrane’s transport properties to be modulated in-situ in response to excursions that are otherwise detrimental to the battery’s cycle-life. There remains much to be learned about the origins of their adaptive and dynamic properties, and how these feed back across multiple length and timescales in the electrochemical cell.

2:30 PM ES01.07.02
Electrostatically Tuned Microdomain Morphology and Phase-Dependent Ion Transport Anisotropy in Single-Ion Conducting Block Copolyelectrolytes

Chenxi Zhai1, Huanhuan Zhou1, Teng Gao1, Lingling Zhao1 and Shangchao Lin1,2; 1Mechanical Engineering, Florida State University, Tallahassee, Florida, United States; 2Materials Science and Engineering, Florida State University, Tallahassee, Florida, United States; 3Energy & Environment, Southeast University, Nanjing, China.

Block copolyelectrolytes are solid-state single-ion conductors which phase separate into ubiquitous microdomains to enable both high ion transference number and structural integrity. Ion transport in these charged block copolymers highly depends on the nanoscale microdomain morphology; however, the influence of electrostatic interactions on morphology and ion diffusion pathways in block copolyelectrolytes remains an obscure feature. In this paper, we systematically predict the phase diagram and morphology of diblock copolyelectrolytes using a modified dissipative particle dynamics simulation framework, considering both explicit electrostatic interactions and ion diffusion dynamics. Various experimentally controllable conditions are considered here, including block volume fraction, Flory–Huggins parameter, block charge fraction or ion concentration, and dielectric constant. Boundaries for microphase transitions are identified based on the computed structure factors, mimicking small-angle X-ray scattering patterns. Furthermore, we develop a novel “diffusivity tensor” approach to predict the degree of anisotropy in ion diffusivity along the principal microdomain orientations, which leads to high-throughput mapping of phase-dependent ion transport properties. Inclusion of ions leads to a significant leftward and upward shift of the phase diagram due to ion-induced excluded volume, increased entropy of mixing, and reduced interfacial tension between dissimilar blocks. Interestingly, we discover that the inverse topology gyroid and cylindrical phases are ideal candidates for solid-state electrolytes in metal-ion batteries. These inverse phases exhibit an optimal combination of high ion conductivity, well-percolated diffusion pathways, and mechanical robustness. Finally, we find that higher dielectric constants can lead to higher ion diffusivity by reducing electrostatic cohesion between the charged block and counterions to facilitate ion diffusion across block microdomain interfaces. This work significantly expands the design space for emerging block copolyelectrolytes and motivates future efforts to explore inverse phases to avoid engineering hurdles of aligning microdomains or removing grain boundaries.

2:45 PM BREAK

3:15 PM ES01.07.03
Crossover Mechanisms in Polymer Membranes for Redox Flow Batteries

Leeo J. Small, Harry D. Pratt, Cy Fujimoto and Travis M. Anderson; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Redox flow batteries (RFBs) offer a scalable solution to grid scale energy storage. The polymer membrane in the RFB that separates the anolyte and catholyte is often underappreciated, preventing mixing of anolyte and catholyte while enabling counter-ion transport. During typical RFB operation, many membranes allow not only inert counter-ions, but also redox-active species to be transported through them. This unwanted transport of redox-active species, called crossover, effectively robs the battery of capacity and decreases performance. Understanding the fundamental mechanisms by which redox-active species are transported through the membrane is essential to designing next generation membrane materials. Here we discuss our recent progress evaluating the performance of several commercial and custom-made membranes using model aqueous and non-aqueous RFB chemistries. We demonstrate how fundamental membrane materials properties can be related to overall RFB performance. Trade-offs in membrane design (e.g. high conductivity vs. high diffusion) are shown to influence crossover mechanisms and overall RFB performance, offering insight to improving the performance of RFBs for grid scale energy storage.


3:30 PM +ES01.07.04
Multifunctional Hydrogels for Energy Storage

Guihua Yu; The University of Texas at Austin, Austin, Texas, United States.

It is the reason why CEA-Liten and Solvay has engaged a large R&D program to propose a new safer and durable lithium battery system constituted of a hybrid polymer membrane and two gelled electrodes. The gelled character of the electrodes, i.e. the retention of the electrolyte in the electrode microstructure is favored by the use of a Solvay proprietary poly(vinylidene fluoride) based polymer as binder, capable to trap a lithium ion conducting organic solution. Specifically designed it ensures high adhesion, it allows obtaining adhesive microporous electrodes to metallic (Al or Cu based) current collector with porosity fully filled by carbonate based electrolyte. The method for preparing such gelled electrodes was developed in acetonitrile media, according to a three-step procedure similar to classical electrodes of Li-ion cell. Thus, after dispersion of the powder compounds in acetonitrile in presence of the electrolyte, the electrode ink is coated, dried and densified by calendaring in air under appropriate conditions. Prepared with ethylene carbonate / Propylene Carbonate (EC:PC 1:1) solution containing bis(trifluoromethanesulfonyl)imide lithium salt, LiTFSI (1M) or lithium hexafluorophosphate, LiPF6 (1M) at the labscale but also in continuous mode, the gelled graphite (Cgr) based or LiNi0.5Mn0.3Co0.2O2 (NMC) based electrodes exhibit regular surface, homogenous thickness with low roughness and good adhesion. In addition, its properties of flexibility and cohesion allow its implementation in wound roll of several meters.

Moreover, assembled with hybrid polymer membrane without any addition of complementary electrolyte, the gelled electrodes work successfully at various discharge rates, even at high rates and exhibit a very stable behavior with very long cyclife.
Hydrogels have become an appealing material platform for energy storage technologies. Developing hydrogels with enhanced physicochemical properties, such as mechanical strength, flexibility, dimensional stability, and fast charge transport, offers new opportunities for significantly improving the performance of energy storage devices. In this talk, I will discuss recent innovations in rational design and synthesis of hydrogels with diverse features, including stimuli-responsive, self-healing, and highly stretchable for next-generation electrochemical devices. I will then focus on how hydrogels have been integrated into energy storage systems, highlighting exciting examples that demonstrate the versatility of hydrogel materials in terms of tailorable architectures, conductive nanostructures, 3D frameworks and multi-functionalities.

4:00 PM ES01.07.05
Liquefied Gas Electrolytes for Low-Temperature Li-Metal Batteries
Yangyang Chen Yang1, Davies Dai2, Yiwei Yin1, Chengeng Fang1, Jungwoo Lee1,2, Xuefeng Wang2, Cyrus Rustgi1,3 and Y. Shirley Meng1,2,3; 1Materials Science and Engineering Program, University of California, San Diego, La Jolla, California, United States; 2Department of Nano Engineering, University of California, San Diego, La Jolla, California, United States; 3South 8 Technologies, San Diego, California, United States.

The key to enabling high-energy-density lithium (Li) metal batteries is the development of electrolyte for resolving Li metal challenges, in particular, the dendritic growth and low coulombic efficiency. The low-temperature operation is a large challenge for lithium-ion batteries, resulting from the sluggish diffusion, including the reduced electrolyte conductivity by electrolyte freezing, largely increased SEI resistances and the limited Li-ion diffusivity in the electrodes. However, there has been little change of electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. Systems using fluoromethane-based liquefied gas electrolytes demonstrate remarkable rate capability (up to 10 mA cm⁻²) and excellent dendrite-free long-term (>500 cycles) cycling of Li metal anodes with a high coulombic efficiency of up to 99.9%. Both the rate and cycling performance are well maintained at a low temperature down to -60 °C. The superior performance is ascribed to the formation of a compacted Li metal deposition microstructure and a conductive, stable solid electrolyte interphase (SEI). This study opens up a promising avenue toward the applications of high-energy-density Li metal batteries.

4:15 PM ES01.07.06
Poly (aryl ether sulfone) Network Copolymer Membranes for Direct Methanol Fuel Cell (DMFC) Applications
Ende Can and Esra Yilmaz; Chemical Engineering, Yeditepe University, Istanbul, Turkey.

Fuel cells, which are electrochemical devices that convert the chemical energy into electrical energy have been considered as an alternative to existing power systems with high energy density, stable mode of operation and low pollution to environment. Fuel cells are most commonly classified by the type of electrolyte used in the cell. Proton exchange membrane fuel cells (PEMFCs), also classified as polymer electrolyte fuel cells (PEFCs) are low temperature fuel cells which represent a promising potential for portable devices, automobiles and power sources. The anode reactant is gaseous hydrogen in PEMFCs. Direct methanol fuel cell (DMFC) is a subgroup of PEMFCs and differs from it by the anode reactant which is liquid water and methanol. For DMFCs, a fuel reformer is not necessary as the platinum-ruthenium catalyst used in the DMFC anode can remove the hydrogen from liquid methanol. Use of methanol as a fuel has various advantages as it has a relatively high energy density, it is inexpensive, and in addition it can be easily stored and transported. On the other hand, DMFCs can be utilized in applications with limited power requirements, like mobile electronic devices or chargers and portable power packs for materials handling vehicles. The key component of a DMFC is the polymer electrolyte membrane (PEM) that acts as a mechanical separator between anode and cathode and demonstrates important functionalities like proton transport and methanol barrier. In this study, membranes of cross-linked sulfonated poly(aryl ether sulfone) derivatives were prepared and characterized for use in Direct Methanol Fuel Cell (DMFCs). For this purpose, partially sulfonated poly(aryl ether sulfone) (PESS) was synthesized and modified through an addition reaction of glycicyl methacrylate to the hydroxyl ends of the PESS polymer. The synthesized pre-polymer (PESSGMA) was then cross-linked via homo-polymerization and the oxidative polymerization with styrene and changing amounts of vinyl phosphonic acid (VPA). Crosslinking of the PESS polymer significantly decreased the swelling in water, ion exchange capacity, and the proton conductivity as well as the methanol permeability. The incorporation of VPA in the PESSGMA network on the other hand, increased the proton conductivity and the oxidative polymerization while keeping the outstanding resistance to methanol cross over which was significantly higher than that of the commercial Nafion membrane. Membranes of PESSGMA network copolymers with VPA showed Tg values in the range of 94 °C - 114 °C, water uptake values below 32% at 80 °C, proton conductivity values in the range of 16-32 mS cm⁻¹ and methanol permeability values in the range of 6.5x10⁻⁹ - 1.92x10⁻⁹ cm² s⁻¹ at 60°C [1]. In addition results of Fenton’s test showed that these membranes possessed excellent oxidative stability in a strongly oxidizing environment. Hence, the PESSGMA-VPA and PESSGMA-STY-VPA copolymer membranes developed in this study exhibit a high potential for use in DMFC applications. Moreover, these membranes can alternatively be useful in organic redox flow batteries as the proton-conducting polymer electrolyte membrane that keeps the reductive couples apart. The proton conductive PESSGMA-VPA network copolymer membranes should resist the cross-over of polar organic molecules like methanol and therefore have the capability to find applications in organic redox flow batteries.


4:30 PM ES01.07.07
Highly Conductive Polybenzimidazole Based Membranes Applied to All Vanadium Redox Flow Batteries
Lihui Wang1, Andrew Pingitore1, Wei Xie1, Yang Zhiew1, Mike L. Perry2 and Brian Benicewicz1; 1Univ of South Carolina, Columbia, South Carolina, United States; 2United Technologies Research Center, East Hartford, Connecticut, United States.

A series of polybenzimidazole (PBI) membranes were synthesized using sol-gel process and modified for all vanadium redox flow batteries (VRFB). These membranes demonstrated not only a high in-situ and ex-situ stability in concentrated sulfuric acid and in oxidative vanadium (V) solutions but also exhibited high conductivities and low performance degradation during in-cell testing for the ‘conventionally imbibed’ meta-polybenzimidazole (m-PBI) membranes cast from N,N’-dimethylacetamide (DMAc) solutions. The PBI membrane doped with 2.6 M H₂SO₄ shows a proton conductivity of 390 mS/cm at room temperature and VO²⁻ permeability as 2.30E-08 cm²/s. Different strategies were anticipated to block the porous structure of PBI membranes and further decrease vanadium ion permeability while maintaining the high proton conductivity. A VRFB operated with the modified PBI membrane shows over 98% coulombic efficiency under a large range of applied cell cycling current densities from 100 to 450 mA/cm².

SESSION ES01.08: Membranes and Electrolytes for Rechargeable Batteries II
Session Chair: Wu Xu
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 126 A

8:30 AM *ES01.08.01
Stable High-Voltage Lithium Metal Batteries Enabled by Organic Ether Electrolytes
Wu Xu1, Xiaodi Ren1, Shuhong Jiao1,2 and Ji-Guang Zhang1,2; 1Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States; 2Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, China.

The state-of-the-art lithium (Li)-ion batteries are approaching their energy density limit and cannot meet the fast increasing demand for higher energy density requirements. Due to the ultrahigh theoretical specific capacity (3,860 mAh g⁻¹) and the extremely low standard electrochemical redox potential (-3.040 V) of Li metal, it has long been regarded as an ideal anode material. The research and development of rechargeable Li metal batteries has therefore been revived in recent years. However, the big challenges related to Li metal anode, such as the safety issues due to the formation of metallic Li dendrites during repeated charge/discharge cycles and the short cycle life because of low Li Coulombic efficiency (CE), have not been completely solved and there is still a long way to go for the commercialization of rechargeable Li metal batteries. Many approaches have been reported to address the above challenges to Li metal anode and Li metal batteries, and many achievements have been reported recently. Among the reported strategies, the electrolyte design is one of the most effective and facile approaches to improve Li CE and cycling stability. Organic ether solvents have been found to be more stable with Li metal
Electrodeposition in Viscoelastic Polymer Aqueous Electrolyte

Electrodeposition plays an important role in electrochemical storage technologies based on batteries. It should be carefully managed to facilitate safe and stable operations in a broad range of conditions. In liquid electrolyte, deposition is subject to a variety of hydrodynamic and morphological instabilities, leading to a strong convective process near the interfaces. In many situations, the instabilities are problematic as the produced complex flows cause dendrite formation at planar interfaces, which is linked to the failure of microcircuits and overlimiting conductance.

This study focuses on the effects of aqueous viscoelastic electrolyte and the buoyancy force on the electrodeposition instabilities. By introducing a small amount of the polymers, the viscosity of the electrolyte largely increases without compromising ionic mobility. As a result, the voltage window of limiting current increases in the viscoelastic aqueous electrolyte. In the gravitationally unstable configuration, the variation of salt density leads to a Rayleigh-Bernard flow that increases the current. In this case, the influence of individual factors of the buoyancy effect is studied in the viscoelastic electrolyte system. And the qualitative and quantitative comparison with theoretical and simulation studies are performed to help clarify the mechanisms.

Organic Electrolytes in Promoting the Performance of Lithium-Ion and Sulfur-Based Batteries—X-Ray Spectroscopy Studies

Organic electrolyte is the key part in battery, but for various types of battery the requirements are different. An intercalation battery may prefer the formation of protective but ionic conducting solid-electrolyte interphase that is usually decomposed from the organic electrolytes, while the sulfur-based batteries need the electrolytes to suppress the formation of polysulfides. How to develop suitable electrolytes still remain technically challenging. In my group, we take the in situ operando view to check the performance of electrolytes and electrodes using X-ray absorption spectroscopy at both hard and soft X-ray regions. These element-specific methods enable us to examine the light elements in electrolytes and heavy elements in electrodes for comprehensive understanding. I will illustrate examples in lithium-ion batteries and lithium/magnesium-sulfur batteries to demonstrate how electrolyte can promote/inhibit the reactions.

Next generation electrochemical energy storage systems based on divalent metal cations occupy a new frontier of research and development efforts related to materials chemistry and design. High energy density batteries based on Mg or Ca metal anodes are yet to be realized due to problems associated with the stability and ion transport properties of organic electrolytes and insertion cathodes. In this presentation we will discuss results related to controlling Mg$^{2+}$ electrolyte properties via tuning of the organic solvent structure. While the role of competitive solvent and anion interactions in defining the properties of univalent organic electrolyte systems has received considerable investigation, such knowledge is still emergent in the divalent electrolyte field. This presentation will serve as a discussion of our recent findings on how the elemental solvent or co-solvent (e.g. glymes, cyclic ethers) structure defines stable Mg$^{2+}$ anion solvation populations, which in turn determine critical electrolyte performance attributes including ionic conductivity and Mg metal plating efficiency. Specifically, we will present electrochemical characterization of several inorganic and organic Mg-salts including MgCl$_2$, MgF$_2$H$_2$, Mg(CB$_2$H$_2$)$_2$, and Mg(BF$_4$)$_2$ across a systematic variation of etheral solvents along with characterization of the resulting solvation environments through solution spectroscopies including Raman, NMR, and X-ray absorption spectroscopy (XAS). These experimental results are further augmented with the aid of density functional theory and molecular dynamics simulations, providing insight into how the solution and interfacial chemistry regulates the behavior of Mg$^{2+}$ electrolyte systems.

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Decomposition of Phosphorus-Containing Additives at a Charged NMC Surface—Atomistic Modeling Insights

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Lithium-ion batteries (LiBs) have been predominant in electric vehicles and electronic devices applications because of their unparalleled combination of energy density and reasonable cost. Stabilizing the cathode/electrolyte interface at high voltage is necessary to achieve higher capacities while still maintaining capacity retention. However, the traditional organic carbonate-based electrolytes are not stable at these high voltages, new strategies must be adopted to stabilize this interface. One such strategy is through the use of inorganic electrolytes and insertion cathodes. In this presentation we will discuss results related to controlling Mg$^{2+}$ electrolyte properties via tuning of the organic solvent structure. While the role of competitive solvent and anion interactions in defining the properties of univalent organic electrolyte systems has received considerable investigation, such knowledge is still emergent in the divalent electrolyte field. This presentation will serve as a discussion of our recent findings on how the elemental solvent or co-solvent (e.g. glymes, cyclic ethers) structure defines stable Mg$^{2+}$ anion solvation populations, which in turn determine critical electrolyte performance attributes including ionic conductivity and Mg metal plating efficiency. Specifically, we will present electrochemical characterization of several inorganic and organic Mg-salts including MgCl$_2$, MgF$_2$H$_2$, Mg(CB$_2$H$_2$)$_2$, and Mg(BF$_4$)$_2$ across a systematic variation of etheral solvents along with characterization of the resulting solvation environments through solution spectroscopies including Raman, NMR, and X-ray absorption spectroscopy (XAS). These experimental results are further augmented with the aid of density functional theory and molecular dynamics simulations, providing insight into how the solution and interfacial chemistry regulates the behavior of Mg$^{2+}$ electrolyte systems.

Enabling High Voltage NMC/Gr Cell Performance with a Polyfluorinated Electrolyte Blend

Enabling High Voltage NMC/Gr Cell Performance with a Polyfluorinated Electrolyte Blend

Enabling high-energy, high-voltage lithium-ion batteries requires the detection, measurement and mitigation of degradation processes that decrease both energy- and power-density during prolonged cycling. This presentation will discuss different diagnostic methods of high-voltage reactivity with LiNi$_{0.3}$Mn$_{0.3}$Co$_{0.4}$O$_2$ (NMC532) cathodes, as well as the use of a high-voltage electrolyte (polyfluorinated electrolyte blend of difluoroethylene carbonate and hexafluoro-2-dimethylcyclopentene, referred to as FE-3) to increase stability and cycling performance. FE-3 leads to less oxygen loss from the surface of the NMC532 structure, less surface degradation, and a lower parasitic oxidation current, compared to the traditional organic carbonate electrolyte. On the graphite anode, FE-3 shows superior passivation behavior, and graphite electrodes preformed with FE-3 show excellent capacity retention and lower impedance rise and transition metal dissolution when cycled at high voltage with the traditional organic carbonate electrolyte and an NMC532 cathode. This work shows that soluble reduction products from an incompletely passivated graphite anode are major contributors to cell impedance rise at high voltage.
A Facile Approach to Generate Highly Active and Durable Heterogeneous Electrocatalyst for the Oxygen-Evolving Reaction from Ni-Loaded, Metal-Organic Framework-Graphene Composite—In Situ Electrospinning to Fabricate High Throughput Electrocatalyst Process Mohamed Hassan1, Ahmed Soliman2, Woroud Elmehelmy1, Arwa Abugable1, Stavros Karakalos1, Mady Elibari2, Abdou Hassani1 and Mohamed H. Alkordi3, 1Center for Materials Science, Zewail City of Science and Technology, Giza, Egypt; 2Department of Chemistry and Materials Science, Aalto University, Aalto, Finland; 3College of Engineering and Computing, University of South Carolina, Columbia, South Carolina, United States; Condensed Matter Physics Department, Jozef Stefan Institute, Ljubljana, Slovenia.

We report on a novel approach through which metal-organic framework constructed on graphene platelets is converted, in situ, into highly active and durable water splitting electrocatalyst. This approach to construct highly active and durable Ni(OH)2 nanoparticle/graphene hybrid electrocatalyst utilized the Ni-loaded, graphene-supported metal-organic framework (UIO-66-NH2-Ni/G) as a sacrificial pre-catalyst to generate the true catalyst, in situ, under the electrolysis conditions. The resulting nanocatalyst was shown to enclose Ni(OH)2 nanoparticles imbedded within hydrous zirconia and deposited on top of G platelets, demonstrating a high electrocatalytic activity towards oxygen-evolution reaction (ηO2 = 0.38 V vs. RHE) and highly durable catalyst. This strategy can potentially be extended to several other systems as a less energy-consuming alternative to the commonly utilized pyrolysis pathway to generate electrocatalysts from MOFs.

11:15 AM ES01.08.08
Single-Ion Conducting Polymer Coatings for Mitigation of the Polysulfide Shuttle Effect in Metal-Sulfur Rechargeable Batteries Hunter Ford, Peng He and Jennifer Schaefer; University of Notre Dame, Notre Dame, Indiana, United States.

The development of new rechargeable battery systems employing novel chemistries is imperative to meet the increasing energy storage demands of emerging technologies. Metal-sulfur batteries are a promising set of chemistries for moving beyond lithium-ion, owing to the widespread abundance of sulfur and the high theoretical energy density of many metal-sulfur couples. However, it is well known that metal-sulfur systems suffer poor performance as a result of the polysulfide shuttle effect. Building on previous work demonstrating the delicate balance of ion transport in a functional interlayer1, i.e. allowing cation transport while minimizing polysulfide transport, thin single-ion conducting polymer coatings are investigated for their ability to mitigate the polysulfide shuttle effect in lithium- and magnesium-sulfur cells. Relative to a bulk polymer layer, a thin coating contributes significantly less to the total cation conduction resistance observed in the cell. The decreased resistance stemming from a thin layer design enables exploration of a polymer composition space that favors polysulfide restriction at the expense of cationic conduction, such as the use of highly crosslinked ionomer networks in which the primary mechanism of cation conduction is solid state. Differences in solid state Li+ and Mg2+ conduction present the need for polymer compositions tailored specifically to the cation identity. Relationships between cell performance and a given ionomer chemical composition, structure, and transport mechanisms are determined with a combination of ex situ characterization techniques and full cell cycling.

Hunter O. Ford, Laura C. Merrill, Peng He, Sunil P. Upadhyay, and Jennifer L. Schaefer Cross-Linked Ionomer Gel Separators for Polysulfide Shuttle Mitigation in Magnesium–Sulfur Batteries: Elucidation of Structure–Property Relationships Macromolecules Article ASAP

2:00 PM *ES01.09.01
Organic Derived Nanomaterials for Emerging Energy Storage Jiangang Mai; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhuan University of Technology, Wuhuan, China.

Nanomaterials can offer large surface area, facile strain relaxation upon cycling and efficient electron transport pathway to achieve high electrochemical performance. Organic compounds have achieved immense priority over inorganic materials for their manageable structures, suitable operating voltage and abundance as well as renewability. We have synthesized graphene oxide-wrapped organic dipotassium terephthalate (K2TP)(GO) hollow microcruds using an abundant and renewable organic resource. During the potassitation process, the crystalline phase of K2TP gradually transformed into amorphous K2TP. They demonstrate enhanced potassium storage performance compared to bulk K2TP, which mainly ascribed to the fast K+ ion transfer kinetics, high electronic conductivity and short diffusion distance. In addition, we have also developed a facile and high-yield strategy for the oriented formation of CNTs from metal-organic frameworks (MOFs). The appropriate graphitic N doping and the confined metal nanoparticles in CNTs both increase the densities of states near the Fermi level and reduce the work function, hence efficiently enhancing its oxygen reduction activity. Moreover, we also obtained thio-cyanato-functionalized SiO2 (SCN-SiO2) micropheres through the hydrolysis and condensation of organic silicon source (3-thiocyanatopropyltrimethoxysilane). A vinyl-functionalized SiO2(CH2=CH-SiO2) layer and a thiol-functionalized SiO2 (SH-SiO2) layer was also coated onto the surface of SCN-SiO2 in sequence. The rationally designed yolk@shell structured SiO2/C composite anode materials manifest high specific capacity, excellent rate capability and superior cycling stability in lithium storage. Our work presented here can inspire new thought in constructing novel organic compound structures and accelerate the development of energy storage applications.

2:30 PM ES01.09.02
Progressively Releasing Potassium Ions via Electrospun Nafion-Based Separator for Lithium Metal Batteries Mengfei Hu and Donghui Long; East China University of Science and Technology, Shanghai, China.

High-energy-density lithium metal batteries have aroused widespread interest due to the high theoretical capacity. However, uncontrolled dendrite formation and infinite volume expansion hinder the practical application of lithium metal anode. Herein, we develop a new strategy to make adsorption induction and ionic intervention well-combined to modulate the Li deposition behavior. A K+-doped Nafion nanofiber separator, having abundant lithophilic groups and porous framework is electrospun. It can provide high affinity with electrolyte and large electrolyte uptake. It also provides uniform pathway for lithium ions transportation, and a parclose for the stress of volumetric change during lithium plating/stripping. Moreover, it can release K+ as an inhibitor to prevent aggregation of Li ions by forming an electrostatic shielding on the surface of electrode. As a result, the functional separator can guide uniform lithium deposition, leading to high Coulombic efficiency (98.5%) and low overpotential (~15 mV) in symmetric cells with long lifespan. This work shed the dawn of the research on the multi-functional electrospun separators for dendrite-free lithium metal batteries.

2:45 PM ES01.09.03
Heterocyclic N-Rich Salts for Li Metal Battery Mxung-Jin Lee, Victor Roev, Min Sik Park, Hongsoo Choi and Dongmin Im; Samsung Advanced Institute of Technology, Suwon, Korea (the Republic of).

In order to realize a perfect solid polymer electrolyte (SPE) concept for lithium batteries, there is a need for lithium new salts. The new salts must be cheap and stable and able to provide a large number of charge carriers to meet the demands on ionic conductivity. In polymer electrolytes, the salt concentration is usually high, thus an important factor affecting the ion conductivity is the equilibrium between “free” anions, ion pairs, and higher aggregates, which tend to form in concentrated electrolytes. Weakly cation coordinating anions, such as the triflate, perchlorate or the “imide”/TFSI anions are therefore good candidates for SPE lithium salts. The chemistry of new salts employed in SPEs, today, is in many cases based on the electro reduction power of fluoride atoms. Lithium salts with organic anions, heterocyclic aromatic anions are considered as candidates of choice for this application because they are expected to combine good ionic conductivity and wide electrochemical stability. Especially, those organic salts have electrochemical stability toward Li metal anode and have a good efficiency. A high value of the lithium ion transference number is also desirable. Much less is published on the corresponding triazolate anion; P2I stacking and association of the flat aromatic molecules are probably responsible for the depressed mobility of the anion, thus accounting for the enhancement in the cation transference number.

3:00 PM ES01.09.04

Covalent Organic Nanosheets(CONs) as an Effective Storage Materials as Sodium-Ion Battery Electrodes Min-Sung Kim, Won-Jae Lee and Jin Kuen Park; 1Hankuk University of Foreign Studies, Yongin, Korea (the Republic of); 2Kyungpook National University, Daegu, Korea (the Republic of).

Here, we demonstrated the structure-related energy storage performance of covalent organic nanosheets (CONs) synthesized by Stille cross-coupling under conventional reflux and solvothermal conditions, displaying that the specific surface area and self-assembled morphology of the nanosheets can be effective regulated by a deliberate choice of the synthetic method and monomer combination. The Sodium-ion storage capacity in the mentioned above CONs could be increased by elevating their conductivity of charge carriers via enforcement of a network polymer backbone planarity or by enhancing their specific surface area while maintaining polymer structure constitution. Comparing the anodes manufactured by combining each synthesized CONs, the electrodes based on CON-16 showed the highest cycling performance and rate capability, maintaining a reversible discharge capacity of up to 250mAh/g after 30 cycles at a current density of 100 ma/g.

3:15 PM ES01.09.05
Impact of Thin Coating Layers on Metal Dissolution for Battery Applications Yufang He, Yaqi Zhu, Xinhua Liang and Jonghyun Park; Missouri University of Science and Technology, Rolla, Missouri, United States.

Dissolution of active material is one of the primary reasons for capacity fade in lithium-ion batteries, particularly at elevated temperatures. Ultra-thin coated cathode particles via Atomic Layer Deposition (ALD) exhibit superior battery performance over bare particles. However, we have observed a coating layer can decrease or accelerate the metal dissolution depending on the coating materials. For instance, an ultra-thin CeO2 coating intensifies Mn dissolution of lithium manganese oxide cathode material during cycling of battery, whereas ultra-thin AI2O3 coating tends to inhibit Mn dissolution. A detailed study of Density Functional Theory (DFT) has been carried out to illustrate the experimental observations. First, the manganese vacancy formation energy is calculated, along with the bonding strengths of Mn-O of uncoated, Al2O3 coated, and CeO2 coated particles via Crystal Orbital Overlap Populations (COOP) calculations. Further, the projected density of state calculation of Mn is used to confirm the electronic occupancy of Mn atom for each case. Surprisingly, the atomic analysis is consistent with the experimental observations. This finding can provide new insights into ALD coatings and their impact on metal dissolution in cathode materials.

SYMPOSIUM ES02

Next-Generation Intercalation Batteries
April 23 - April 25, 2019

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SESSION ES02.01: Oxygen Redox Chemistry I
Session Chairs: Y. Shirley Meng and Louis Piper
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 126 C

10:30 AM ES02.01.01
Structural Origin of Oxygen Redox Reversibility in Li-Rich Layered Oxide Cathodes for Li-Ion Batteries Chong Yin, 1, 2 Bao Qiu, 1 Jiaming Bai, 1 Zhaoping Liu 2 and Feng Wang; 1 Brookhaven National Laboratory, New York, New York, United States; 2 Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China.

Lithium-rich (LR) layered oxides are among the most promising high-energy cathode candidates for next-generation Li-ion batteries LIBs, with excess capacity enabled by oxygen redox (OR). Recent studies show that their actual OR reversibility is largely determined by the local structural ordering, especially stacking faults. However, due to the challenge in quantitative determination of stacking faults, there has been intense debate on how stacking faults affect the OR in LR layered oxides. In this work, we made quantitative analysis of the dependence of stacking faults on the Li contents in Li1+xNi0.13Co0.13Mn0.54O2 through synchrotron X-ray and neutron diffraction measurements coupled with structure refinements using FAULTS program. Results from the refinements using a composite 2-phase model (C2-m and R-3m phases) match well with experimental data, and so allowing us to make quantitative investigation on the correlation between the stacking faults and OR reversibility. Finding from this study, along with its implication to rational design of LR layered oxide cathodes will be discussed.

10:45 AM ES02.01.02
First-Principles Modeling Of Peroxo-/Superoxo-Like O-O Dimers for High Capacity Cathode Materials of Lithium-Ion Batteries Zhenlian Chen1, 2, Xiao C. Zeng2 and Jun Li1; 1NIMTE, Chinese Academy of Sciences, Ningbo, China; 2Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

High capacity cathode material is key to meet high expectation on lithium ion battery for electrical transportation and smart grids. Cumulatively cationic and anionic redox has been identified as a promise mechanism for next generation cathode materials. The peroxy-/superoxo- like O-O bonding is believed to play important role in anionic redox. 1 However, fundamental understanding of the mechanisms such as the origin and reversibility of peroxy-/superoxo- like O-O dimer is still lacking. So far, theoretical modeling are limited and fail to show peroxy-/superoxo- like O-O dimers in delithiated phases 3, 4, which has been detected during electrochemical performances 5, 6. This talk will show the evolution of peroxy-/superoxo- like O-O dimers during the delithiation process with first-principles modeling. Several morphologies of transition metal peroxy/superoxo complex are found in the partially delithiated phase of Li1+xMnO2 (3/4≤x≤5/4) and oxygen release is predicted to happen when x≥3/2. There are two categories of O-O dimers, one links the MnO6 in same Mn layer or adjacent Mn layers. In the other category, one or two O-O dimer(s) belong(s) to one MnO6 octahedron. The bond length of O-O dimer ranges from 1.25 Å to 1.45 Å, close to the O-O bonds in peroxides and superoxides. Crystal orbital Hamilton population (COHP) analysis shows strong anti-bonding character near to Fermi level and partial charge density indicates π-like anti-bonding charge hole compensate the charge deficiency in delithiated phases during 3/4≤x≤5/4. Surprisingly, peroxy-like
dimers are also found in the second lithium delithiation of polyanionic cathode Li$_2$CoSiO$_4$, challenging the long understanding that only two-electrons conventional cationic redox is recognized in orthogonal silicate cathode family. This study may open a new venture to understand the anionic redox, helpful to rational design of new generation cathode to achieve high energy-density.


11:00 AM ES02.01.03
Reversible Anionic-Cationic Redox in High-Capacity Polyanionic Tetrahedral Silicate Cathode Materials
Xiaohui Zhang, Bojoen Schwarz*, Zhenlian Chen, Cai Shen, Liyuan Huai, Deyu Wang, Zhiheng Zhang, Wenqiang Du, Haitao Zhang, Helmut Ehrenberg* and Jun Li*,
1 Chinese Academy of Sciences, Ningbo, China; 2 Karlsruhe Institute für Technologie, Karlsruhe, Germany.

High capacity cathode materials are a key to the success of high performance lithium ion battery to emerging technologies for electrical transportation and smart grids. Accumulating cationic and anionic redox in transition metal peroxo/superoxo complex has been identified as the key mechanism to achieve superior reversible capacity in multi-lithium compounds. However its associated lattice oxygen releases are a fundamental threat to battery safety and long term performance stability. Here we present a prototype study of Co-Mn lithium silicate composites, in which Co-peroxo/superoxo redox is observed in tetrahedral structured polyanionic materials for high reversible capacity over 230 mAh/g accompanied by zero gas release. Two lithium reactivity and its structure evolution are carefully studied by in operando synchrotron X-ray absorption spectroscopy and powder diffraction. First-principles molecular dynamics are employed to provide the first of its kinds understanding of Co-peroxo/superoxo interaction in the domain of two lithium reactivity. Because of the importance of polyanionic composition in the high safety category of lithium cathode, this study may open a new venture to design rationally a new generation cathode that will achieve high energy-density and high safety simultaneously.

11:15 AM ES02.01.04
Li-Rich Layered Sulfides—An Indirect Way to Better Understand Anionic Redox in Oxides
Saijoy Saha, Gwenaëlle Rousse and Jean-Marie Tarascon,
1 Sorbonne Universités - UPMC Université Paris 06, Paris, France; 2 University Pierre and Marie Curie, Paris, France; 3 Reuseau sur le Stockage Electrochimique de l’Energie (RS2E), Amiens, France.

To comply with the ever-growing demand of energy to power portable electronics and electric vehicles, increasing the energy density of lithium-ion batteries (LIB) has become a major bottleneck. Li-ion battery cathode materials have relied solely on cationic redox reactions, until the recently discovered anionic redox chemistry exchanges, from the approach to design new cathode materials with high energy density, for example, Li$_2$Ni$_{0.2}$Mn$_{0.8}$O$_2$ and Li$_2$Ni$_{0.13}$Mn$_{0.87}$CoO$_{1.9}$ (Li-rich NMC), etc. However, due to certain drawbacks, Li-rich oxides are not far away from commercialization. While intense research is currently devoted to understand this issue, we take a different strategy to contribute to the current understanding of anionic redox, by moving to Li-rich layered sulfides.

While the pure Li$_{1.33}$Ti$_{0.55}$S$_2$ was reported to be electrochemically inactive, we have designed new phases of nominal composition Li$_{1.33}$.05.5Ti$_{0.77}$Fe$_{0.23}$S$_2$ with $y = 0.1 – 0.5$, that are electrochemically active and exhibit an electrochemical activity comparable to Li-rich layered oxides. The voltage profile begins upon charge with a sloped oxidation, associated to the cationic Fe$^{3+}$ oxidation followed by a plateau due to the contribution of the anionic 2$\text{S}^2$$.y$ composition. Maximum reversible discharge capacity up to 245 mAh/g could be obtained for the $y = 0.3$ (Li$_{1.11}$Ti$_{0.78}$Fe$_{0.22}$S$_2$) composition. Via detail study on Li$_{1.11}$Ti$_{0.78}$Fe$_{0.22}$S$_2$, we show a very small voltage hysteresis compared to Li-rich NMC. Concerning the issue of kinetics, oxygen redox is found to be severely affected by sluggish kinetics. However in Li$_{1.11}$Ti$_{0.78}$Fe$_{0.22}$S$_2$, we found that the charge-transfer resistance is very small and remains nearly constant throughout the cycle as opposed to oxides where the resistance builds up drastically with deeper oxidation of oxygen. Despite these positive effects, voltage fading still persists in Li-rich sulfides, though the voltage fade is very less and tends to stabilize after few cycles. The voltage fade is merely ~40 mV. In short we demonstrate that increasing the covalency of metal-ligand bonds by moving to Li-rich sulfides can show paths to mitigate practical bottlenecks of anionic redox.

References:
3. Luo, K. et al. Anion Redox Chemistry in the Cobalt Free 3d Transition Metal Oxide Intercalation Electrode Li[Li 0.2 Ni 0.2 Mn 0.6 ]O 2 Oxidation of O 2– on charging is associated with the generation. J. Am. Chem. Soc 138, 12 (2016).

SESSION ES02.02: Na-Ion Intercalation
Session Chairs: Bryan McCloskey and Benjamin Morgan
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 126 C

1:30 PM *ES02.03.01
Increasing the Energy Densities of Na-Ion Batteries—Fundamental and Practical Aspects
Saritha Maryappan, Qing Wang and Jean-Marie Tarascon,
1 CNRS3459, Reuseau sur le Stockage Electrochimique de l’Energie (RS2E), Amiens, France; 2 Sorbonne Université - UPMC Université Paris 06, Paris, France.

Batteries, as one of the most versatile energy storage device, are key enablers for the decarbonisation of both the transport and power sector. Li-ion batteries being light weight and capable of providing high energy density have conquered the transport sector, therefore, there is a sorely need for low cost batteries for grid applications linked to the use of renewable energies. In this regard, Na-ion battery technology that utilizes more sustainable materials is rapidly developing as a possible alternative to the Li-ion for massive energy storage applications. Several prototype Na-ion batteries using various chemistry have already been demonstrated; the most feasible being the two types of technologies based either on sodium layered oxides Na$_2$MO$_x$ (x ≤ 1, M= transition metal ion(s)) or polyanionic compound such as Na$_2$V$_2$(PO$_4$)$_3$.5F as positive electrode and carbon as negative electrode. Nevertheless, both technologies suffer with poor specific energy in comparison to their lithium counterparts, the major limitation being the poor achievable capacity and/or the redox voltage of the positive electrode. The polyanionic phases suffer high molecular weight and hence poor capacity, while the sodium layered oxides cannot achieve their theoretical capacity due to their structural instability. In order to increase the specific energy of the sodium ion cells, at first, it is essential to understand the origin of such limitations. Hence, we have studied the poly anionic Na$_2$V$_2$(PO$_4$)$_3$.5F and several sodium layered oxides systems and bench marked their performances in practical Na-ion full cells. The results will be discussed by considering the fundamental aspects such as structure-stability-electrochemical performance relationships of the electrode material, moisture stability, interfacial reactivity and thermal stability of the charged electrode, hence safety of the Na-ion cells. Finally, a new material design approach will be discussed with the hope that they will help the battery community to develop high capacity electrode materials that can overpass the limitations of the present generation sodium ion batteries.

References:


2:00 PM ES02.03.02 Solution Phase Na3V2PO4F7 Nanoparticles Synthesis for High Power and High Energy Density Sodium-Ion Battery [Hyungseok Kim1,2, Jesse S. Ko1 and Bruce S. Dunn1;1Univ of California-Los Angeles, Beaverton, Oregon, United States; 2Center for Energy Storage Research, KIST, Seoul, Korea (the Republic of)].

Room temperature Na-ion batteries are highly considered as an alternative technology to Li-ion batteries and are projected to be manufactured at a much lower cost. The development of high power high energy density Na-ion batteries is contingent upon carefully choosing high performance positive and negative electrodes. Among the candidate phosphate materials, sodium vanadium fluorophosphate (Na3V2PO4F7) has gained considerable interest with its high redox potential of the material (operating voltage ~3.8 V vs. Na/Na+) and high theoretical capacity (130 mAh g⁻¹). To date, the primary synthesis approach for obtaining Na3V2PO4F7 is high temperature solid state reaction, however, to drive down the cost of SIBs, it would be beneficial to use a low cost and low energy consumption synthesis approach. In this study, we aim to implement a two-step solution phase synthesis (Pechini and hydrothermal) to consume less energy and minimize our impact on the environment to prepare Na3V2PO4F7 nanoparticle which is demonstrated as a high-rate high cycle life positive electrode material. At various charging rates, Na3V2PO4F7 achieved a high capacity of 130 mAh g⁻¹ (1C/10) and up to 80 mAh g⁻¹ (20C). The high rate capability of this material is owed to its nanometric size and its small volume expansion of 3% upon continuous charge-discharge cycles. For these reasons, the cycling behavior showed superior stability where after 100 cycles, 93% of the initial capacity was maintained. Na3V2PO4F7 was then paired with an Sn-reduced graphene oxide negative electrode and in its full cell format achieved a capacity of 115 mAh g⁻¹ (1C) and 68 mAh g⁻¹ (20C). This full cell devices represents a feasible Na-ion battery devices capable of performing on par with commercial Li-ion battery devices (LiCoO2/graphite).

2:15 PM ES02.03.03 Reversible Asymmetric Structure Evolution in NaTMO2 Xin Li; Harvard University, Cambridge, Massachusetts, United States.

Layered sodium transition metal oxide system of NaTMO2 (TM=3d transition metal ions and their mixture) forms a unique materials platform to study the transition metal, oxygen and sodium interactions. Specifically, Fe and Mn, which are not stable in LiTMO3:45 PM [2] Yang & Devereaux, J Power Sources 389, 188 (2018) taken for granted [3].

Oxygen activities, and suggest that oxygen release and lattice oxygen redox are independent processes involved in intercalation batteries, a relationship that has been indiscreetly contributions and its reversibility/cyclability upon electrochemical cycling. The contrasts between different systems provide important clarifications to understand the mysterious beyond X-ray absorption, mRIXS is capable to not only detect the lattice oxygen redox states in battery electrodes [2], but also precisely quantify the lattice oxygen redox activity of Mn and Mn2O3:45 PM [2] Yang & Devereaux, J Power Sources 389, 188 (2018) taken for granted [3].


2:30 PM ES02.03.04 Structural Phase Transitions and Intercalant Ordering in Layered Na- and K-Ion Cathode Materials Jonas Kaufman1, Michael Toriyama2 and Anton Van Der Ven1; 1University of California, Santa Barbara, Santa Barbara, California, United States; 2University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States.

Na- and K-ion batteries offer cheaper, safer alternatives to their Li-ion counterparts. However, additional structural phase transitions upon cycling can lead to faster mechanical degradation in their electrode materials. This is largely because Na+-K+ ions, unlike Li+ ions, are stabilized not only in octahedral coordination but also in prismatic coordination. The latter allows for more complex intercalant orderings due to the availability of a second triangular sublattice. The ordering of Na/K within a given structure greatly influences the voltage profile and ion transport, but can be difficult to resolve experimentally. We have performed first-principles statistical mechanics studies of the layered Na6Co2O7 and K6Co2O7 cathode materials, which exhibit several stable host structures with Na/K in either octahedral or prismatic coordination, related by gliding of CoO2 sheets. Phase stability between these structures and stable Na/K orderings within each structure are presented and compared to experiments. We have identified several “Devil’s staircases” of infinite hierarchical orderings that Na6CoO7 displays over its composition range. K6CoO2 stabilizes similar orderings for intermediate K concentration and a new family of structures with mixed octahedral and prismatic coordination in the same layer at higher concentrations. This mixed phase brings about significant distortions of the CoO2 layers and may facilitate stacking sequence changes at the end of discharge. Potential mechanisms for ion migration in these materials are discussed, as well as implications for Na/K ordering in other layered transition-metal oxides.

2:45 PM BREAK

SESSION ES02.03: Advanced Characterization
Session Chairs: Brent Melot and Louis Piper
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 126 C

3:15 PM *ES02.02.01 mRIXS of Novel Transition-Metal and Oxygen Redox States in Intercalation Batteries Wanli Yang; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Modern developments of ultra-high efficiency imaging of Resonant Inelastic X-ray Scattering (mRIXS) has opened up this fundamental-physics technique for energy material researches with much improved throughput and superior chemical sensitivity beyond conventional spectroscopy. This has become a timely and critical solution to clarify the unusual redox states involved in high energy density materials, including both the cationic and anionic redox reactions in intercalation-type battery electrodes. This presentation will not discuss the complex physics involved in the RIXS process (Tutorial on RIXS planned in this MRS meeting); instead, mRIXS will be introduced from the chemistry point of view to the material science community with examples on both transition-metal and oxygen states. We show that mRIXS could distinguish spectroscopic signatures of a novel MnI+ state in batteries from conventional Mn states, based on the extra dimension of information that is completely missing in x-ray absorption spectroscopy [1]. We then elaborate the problems and challenges of probing oxygen redox reactions in battery electrodes, and demonstrate that, based on the same technical improvement beyond X-ray absorption, mRIXS is capable to not only detect the lattice oxygen redox states in battery electrodes [2], but also precisely quantify the lattice oxygen redox contributions and its reversibility/cyclability upon electrochemical cycling. The contrasts between different systems provide important clarifications to understand the mysterious oxygen activities, and suggest that oxygen release and lattice oxygen redox are independent processes involved in intercalation batteries, a relationship that has been indiscreetly taken for granted [3].


3:45 PM ES02.02.02 How to Obtain Bulk Sensitive Soft X-Ray Spectra Operando From Lithium-Ion Batteries Arthur Braun; Empa, Dübendorf, Switzerland.
Much efforts are undertaken in lithium ion battery research for the identification of processes taking place at the surfaces of electrode materials and components. However, for an intercalation battery also the bulk properties are relevant because the bulk is the host of the lithium ions, notwithstanding that it is the surface where the lithium enters and exits the positive and negative electrodes.

The functionality of the battery electrodes is at large reflected by their electronic structure as it amounts from the crystallographic arrangement of the ions in the electrode materials. In the last 30 years it has become popular to investigate the electronic structure of battery materials and components with x-ray methods, including their *operando* and in *situ* assessment, and including synchrotron radiation centers as the necessary x-ray sources.

It has turned out that the soft x-rays are particularly suited for the elucidation of the electronic structure of the electrodes, particularly the oxide based positive electrodes. It is an unfortunate weakness of the soft x-rays that they have a relatively low penetration depth and thus relatively low information depth. Practically, the attenuation of soft x-rays is around 1 micrometer, whereas the particulates of spinel based cathodes in lithium secondary batteries range in the order of 25 micrometers. Bulk specificity and soft x-rays rule thus each other out. It is thus virtually impossible to get a soft x-ray spectrum at the 3d metal 2p absorption threshold or an oxygen 1s spectrum from the bulk of such industry grade battery material, neither *ex situ* nor in *situ*: unless you use a spectroscopic trick which has matured to real life applicability since only recently.

I will therefore demonstrate how the battery in *situ* cell can be charged and discharged and during this process hard x-rays with 11 keV energy can penetrate the entire cell, and the X-ray Raman contribution from the fluorescence signal can be extracted for example for the Mn 2p features.

It was therefore possible to record a large number of Mn2p soft x-ray multiplets which showed characteristic changes in their relative spectral weight of L2 and L3 peaks while lithium ions are being inserted in the electrode and extracted from the electrode.

Very interestingly it was possible to tickle out the spin states of the Mn ions which shows that there is an intermediate Mn3+ phase which undergoes a high spin and a low spin transition, which hitherto was not known in the condensed state, solid chemistry and battery technology community. The design of the in *situ* cell and the spectroscopic principle of the X-ray Raman method, available only since few years for the battery expert, are explained as well.

References:


4:00 PM ES02.02.03

**Investigation of the Interactions Between Electrodos in Li10Ti2O17 – Based Batteries with Complementary Surface Analysis Techniques (XPS, SAM, ToF-SIMS)** Nicolas Gauthier1, 2, Cécile Courrèges1, Julien Demeaux1, Lionel Goubault2, Cécile Tessier2 and Hervé Martinez1, 1IPREM (UMR5254), Pau, France; 2Recherche, SAFT, Bordeaux, France.

LiTi2O3(2) (LTO)-based negative electrode for lithium-ion batteries is of interest for electrical vehicles due to its safety, low cost and cycling stability [1]. In this study, the effect of the positive electrode on the electrochemical performances of LTO electrodes, in relation with the Solid Electrolyte Interface (SEI) properties, has been investigated [2]. Full cells LTO/LiNi0.5Co0.2Mn0.3O2 (NMC) and LTO/LiMn2O4 (LMO) were cycled at 40°C over 100 cycles and the electrodes were analyzed by XPS, Scanning Auger Microscopy (SAM) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) after one and 100 cycles. Moreover, LTO/LTO symmetrical cells were also analyzed in order to be free of the positive electrode impact. For each system, LTO electrodes are homogeneously covered by surface layers since the first cycle which induces an irreversible capacity loss. This latter is more important for LTO/LMO compared to LTO/NMC and LTO/LTO. Both SEI layers are composed of organic (polyethylene oxides, oxalates) and inorganic species (LiF, phosphates and fluorophosphates) but in different proportions and with different 2D and 3D spatial distributions: fluorne species are detected deeper in the electrode than organic species and in higher quantities for LTO/LMO for instance [3]. Moreover, the SEI is thicker on the LTO electrode when cycled versus LMO compared to NMC and contains small amounts of manganese, homogeneously spread over the surface and deeply inserted in the SEI, which entails an increase of the system impedance. In conclusion, a thick SEI associated with the presence of metallic species could alter the passivating role of the SEI and explain the less efficient electrochemical performance of LTO/LMO cells.

Analysis after cycling at higher voltage are currently in progress to study the evolution of interfacial layers composition and thickness and to better understand the interactions between the two electrode materials.

References:


4:15 PM ES02.02.04

**Tracing Reactivity Through Outgassing in Ni-Rich and Li-Rich Li-Ion Cathode Materials** Bryan D. McCloskey1, 2; 1Chemical Engineering, University of California, Berkeley, Berkeley, California, United States; 2ESDR, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Outgassing of active materials in Li-ion batteries provides a route to quantitatively study degradation processes that occur during cycling. In particular, we are primarily interested in quantifying the individual and coupled decomposition/transformations of the cathode – a lithiated transition metal oxide (TMO) – and the electrolyte – mostly commonly carbonate blends (ethylene carbonate, diethyl carbonate, etc) with lithium hexafluorophosphate (LiPF6) as the salt. Previous observations of high-voltage instabilities include TMO surface reconstruction, transition metal dissolution, electrolyte decomposition, and formation of surface species. However, this picture is still incomplete, with the dependence on electrolyte and TMO composition not yet fully understood. We will present results in which isotopic labeling of 18O in Ni-rich and Li/Mn-rich NMCs is combined with quantitative gas evolution analysis to show that residual solid lithium carbonate (Li2CO3) on the surface of TMOs has a direct impact on electrolyte and electrode degradation. In particular, oxygen release from the TMO lattice is related to the amount of Li2CO3 present in the cathodes. Our results suggest that the role of impurities on interfacial reactivity in batteries is critically important and should be a key parameter considered in similar future studies.
Towards New Thiophosphate and Sulfide Based Solid Electrolytes—Challenges and Perspectives

Bettina V. Lotsch, 1, 2, 3 Nanochemistry, Max Planck Institute for Solid State Research, Stuttgart, Germany; 2 Chemistry, University of Munich (LMU), Munich, Germany.

Fast lithium solid electrolytes are critical components of all-solid-state batteries (SSB) which promise safer operation and higher power and energy densities compared to commercial Li ion batteries. The highly polarizable anionic sulfide sub-lattice of thiophosphates, prominently represented by the tetragonal Li10GeP2S12 (LGPS) family of compounds, provides a rather flat energy 3D landscape with low activation energy paths for lithium ion movement, rendering thiophosphates and, more generally, sulfides, the currently most promising class of materials for the discovery of ultrafast ionic conductivities in solids [1,2,3]. However, LGPS-type thiophosphates are known to readily decompose under ambient conditions, often leading to electronically conductive or insulating products with sluggish Li ion dynamics. In addition, there is an undisputed need to replace the precious Germanium by more earth-abundant elements whilst maintaining high Lithium conductivities of > 1 mS/cm. We will discuss several strategies to tackle these challenges. First, our recent efforts in exploring the solid solution system Li11+2xSi12-xP12-xS12 will be described, which lead to the discovery of new solid electrolytes in the LSiPS family displaying conductivities of > 1 mS/cm [2,4]. While fast in absolute terms, we will show that these materials are in fact glassy ceramics, carrying amorphous side-phases which reduce the apparent Lithium conductivities. Further, the solid solution system Li-Sn-S will be discussed as a source of new sulfide-based superionic Lithium conductors with layered structures. Li11(S1-xSnxS)2 exhibits a lithium ion diffusivity of 6 x 10-15 m2/s at room temperature as determined by pulsed field gradient (PFG) NMR [5,6]. We will show that Li[x]≤(Li11S12SnS2) hydrates in air while maintaining high Li diffusivities and, hence, exhibits greatly improved environmental stability as compared to most sulfide-based solid electrolytes. We will furthermore discuss the exfoliation—restacking of lithium tin sulfide nanosheets into conformal thin films and their strongly hydration-dependent in-plane conductivity, which bodes well for the use of these environmentally robust sulfide solid electrolytes not only in SSBs, but also as solution-processable humidity sensors.

References:
In secondary batteries, the anode/electrolyte interphase plays a key role in the electrochemical performances. As the liquid organic electrolyte undergoes degradation in the electrochemical potential window of a cycling battery, a Solid Electrolyte Interphase (SEI) is formed upon cycling. This interphase layer leads to a double-edged problematic: the formation of the SEI lowers the coulombic efficiency and causes irreversible volume capacity loss, but it also passivates the electrode from the electrolyte and prevents further aging processes. Knowing this, any modification of the SEI should be performed with parsimony as it could break the balance between the positive and negative aspect of the SEI. By synthesizing a chemisorbed thin fluorinated layer upon anode material, we managed to improve the passivating power of the SEI leading to enhanced electrochemical performances. We also demonstrated that very low quantities of fluorine on the active electrode material surface leads to several beneficial effects. We aimed to prospect the influence of the surface fluorination on different aspect of a Li-ion battery, from the active material to the electrolyte interface, thanks to a multi-scale probing approach. The chemical nature of the surface layer was describe by the mean of the XPS, as well as the fluorine distribution on the surface with both AES and SAM. The fluorine has been quantified around 10 at. % of the extreme surface of the Li$_2$Ti$_3$O$_7$ (LTO) material, without diffusion in particles bulks. The bulk and surface-properties of fluorinated LTO (LTO-F) were also investigated by coupling XRD, Raman Spectroscopy and NMR $^1$H, showing no modifications of the crystallographic structure. The influence of the surface fluorination on the electrochemical performance was investigate by galvanostatic cycling and by coupling XPS and SAM on cycled electrodes. We had a specific attention to the impact of the fluorination on the SEI thickness and stability in charge and discharge. Indeed, LTO-F exhibit a new reactivity toward the electrolyte, leading to a thinner and stabilized SEI. Finally, the gas generation of the LTO-F electrodes has been investigate by Gas Chromatography – Mass Spectrometry (GC-MS), as gassing is known to be a roadblock to the commercialization of LTO$^{2-3}$. We demonstrate that the CO$_2$ outgassing is reduced by the surface fluorination.


11:15 AM ES02.05.03

Synthetic Design of Surface Stabilized High-Ni Layered Cathodes for Lithium-Ion Batteries Mingjian Zhang$^{1,2}$, Chong Yin$^1$, Peng Pan$^2$, Jiaming Bai$^1$ and Feng Wang$^{1}$, Brookhaven National Laboratory, Upton, New York, United States; $^3$Peking University, Shenzhen Graduate School, Shenzhen, China.

There has been considerable interest in developing low-cost, high-energy electrodes for batteries. However, synthesizing materials with the desired phases and properties has proven difficult due to the complexity of the reactions involved in chemical synthesis. Additional challenge comes from the fact that synthesis is often undertaken under non-equilibrium conditions and, hence, the process is hard to be predicted by theoretical computations. In situ, real-time probing of synthesis reactions allows for identification of intermediates and determination of thermodynamic/kinetic parameters governing kinetic reaction pathways, thereby enabling synthetic design of materials with desired structure and properties. In this presentation, we will report our recent results from technique development and application to in situ probing and synthetic control of local structural ordering and stoichiometry during synthesis of high-Ni layered LiNi$_{1-x}$(MnCo)$_x$O$_2$. Findings from this study, along with its implication to designing surface-stabilized high-Ni layered oxide cathodes, will be discussed.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office, Contract No. DE-SC0012704.

11:30 AM ES02.05.04

Iron-Based Fluoro(hydroxy)phosphate A$_{2}$FePO$_4$V ($\text{A} = \text{Na}, \text{Li}; \text{V} = \text{F}, \text{OH}$) as Cathode Materials for Aqueous Batteries—Two Case Studies Lalit Sharma$^1$, Shigeto Okada$^2$ and Prabeer Barpanda$^3$, $^1$Materials Research Centre, Indian Institute of Science, Bangalore, Bangalore, India; $^2$Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, Fukuoka, Fukuoka, Japan.

Safety and cost of existing organic electrolytes force us to revisit possible application of aqueous electrolytes. It not only reduces the toxicity but along with fast rate kinetics, it also provides a two-fold increase in the ionic conductivity. However, not all electrode materials are compatible with aqueous electrolytes. Moreover, the limited working potential range to avoid water splitting makes it important to look for efficient and stable electrode materials in aqueous media. In this work, we are presenting two such case studies using earth-abundant Fe-based compounds. First, Na$_2$FePO$_4$F is demonstrated as a cathode material for aqueous sodium-ion batteries where the half-cell delivered a discharge capacity of 85 mAh g$^{-1}$ at 1 mA cm$^{-2}$ current density. Excellent rate kinetics were observed. A full cell was also assembled with Na$_x$FePO$_4$F anode. The Na$_2$FePO$_4$F / Na$_x$Ti$_3$O$_7$ full cell delivered a reversible capacity of 85 mAh g$^{-1}$ working as a 0.8 V battery. The second work is based on LiFePO$_4$OH cathode for aqueous lithium-ion batteries. In half-cell configuration, it delivered a discharge capacity of 140 mAh g$^{-1}$ with very good rate kinetics. Interestingly, it was found to be working in the anodic range for aqueous batteries. The structural characterization along with electrochemical studies will be presented for both case studies.

SESSION ES02.06: Oxygen Redox Chemistry II

Session Chairs: Jatinkumar Rana and Kimberly See

Wednesday Afternoon, April 24, 2019

PCC North, 100 Level, Room 126 C

1:30 PM *ES02.06.01

Evidences of Structural Metastability and Reversibility for Voltage Decay in High-Capacity Li-Rich Layered Cathode Oxides Y. Shirley Meng; University of California, San Diego, La Jolla, California, United States.

The practicality issue of the lithium rich layered oxide materials originate from irreversible structure transformation and voltage decay upon cycling—processes in which defect electrochemistry plays a vital role. Understanding the correlation between defect generation and voltage decay is essential for implementing rational design strategies to improve voltage stability and long term cycling. In this talk I will demonstrate the unique metastable structure of cycled Li-rich layered oxide resulting from defect formation. Modification can be applied to drive the cycled material back to a stable state and subsequently lead to the voltage recovery. This study of structure metastability and reversibility opens up new opportunities for resolving the voltage decay issue in high-capacity layered oxides, more importantly the insights might help the researchers to improve other aspects of the anion redox active materials.

2:00 PM ES02.06.02


The discovery of oxygen redox in Li-rich NMC cathode materials has revived the hopes for high-energy density batteries. [1-2] These materials are derived from the parent compound, Li$_2$MnO$_4$ [3-4], which was initially considered electrochemically inactive due to its Mn$^{4+}$ oxidation state in octahedral coordination. However, reversible capacities were demonstrated for Li$_2$MnO$_4$ in a span of 4.3-4.7 V vs. Li/Li$^+$, and the material稳定性 at high voltages however the exact charge compensation mechanism remains unclear [5]. Recent fundamental studies of oxygen redox have largely focused on 4d and 5d-based model systems, [1] which are prone to less gas evolution. However, elucidating the origin of the excess reversible capacities in LR-rich NMC electrodes requires a fundamental understanding of the nature of oxygen participation within Li$_2$MnO$_4$.

We report the chemical and structural evolution of Li$_2$MnO$_4$ upon cycling using a suite of characterization techniques to evaluate the extent of oxygen release in activating the Mn redox. In addition, oxygen-release is also found to be responsible for gradual structural disordering that occurs upon cycling. These results are discussed in the context of Li-rich NMC electrodes; especially the role of oxygen at the cathode-electrolyte interface [2, 6].

In the pursuit of high energy density Li-ion battery cathodes, Li-rich systems have demonstrated high reversible capacities that are considered accessible through oxygen redox. Investigation into the oxygen redox mechanism and identification of attractive oxygen redox candidates has driven increased utilization of x-ray spectroscopy techniques that directly probe the oxygen environment. In particular, resonant inelastic x-ray scattering (RIXS) at the O K-edge has emerged as a prime technique to provide sensitivity to the oxygen chemical environment. Sharp RIXS features have been observed in a range of transition metal (TM)3d systems, including Li-rich NMC [1], Na2,[Mg0.23Mn0.77]O; [2] and Li1+xMn0.88O2; [3] that are considered signatures of oxidized oxygen. Yet, even for the model Li-rich NMC systems, uncertainty in the interpretation of these RIXS features remains as well as questions on the local environment and long-term stability of oxidized oxygen states.

Here, we focus on the stability of Li[Li0.15Na0.15Mn0.53Co0.13]O2; a model LR-NMC system, at high degrees of delithiation under the x-ray exposure conditions needed to conduct RIXS measurements. Combining xAS and RIXS, our studies demonstrate the sensitivity of surface transition metal and bulk oxygen states to aggressive x-ray beam exposure in LR-NMC systems. In addition to the surface photoreduction of transition metals, we find a strong loss of inherent oxidized oxygen states with x-ray exposure. Our studies demonstrate the utilization of RIXS for the identification of oxidized oxygen states, while providing new insight into the nature of oxidized oxygen environments.

This work was supported as part of NECCES, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0012583

References:
Further, polymer electrolytes composed of ABA-triblock copolymers and [Li(glyme)][TFSA] SILs are proposed to simultaneously achieve high ionic conductivity, thermal stability, and a wide potential window. Different block copolymers, consisting of a SIL-incompatible A segment (polystyrene, PSi) and SIL-compatible B segments (poly(methyl methacrylate) (PMMA) and poly(ethylene oxide) (PEO)) are utilized. The SILs can be solidified with the copolymers through physical crosslinking by the self-assembly of the PST segment. The thermal and electrochemical properties of the polymer electrolytes are significantly affected by the stability of the [Li(glyme)]+ complex in the block copolymer B segments, and the preservation of the SILs contributes to their thermal stabilities and oxidation stabilities greater than 4 V vs. Li/Li+. The [Li(glyme)]+ complex cation is unstable in the PEO matrix, whereas the complex structure of [Li(glyme)]1- is stable in the PMMA-based polymer electrolyte. By using the PMMA-based polymer electrolytes, 4-V class Li batteries with a LiC02O2 cathode and a Li metal anode can be stably operated; in contrast, this is not possible using the PEO-based electrolyte.

4:00 PM ES02.07.02
Suppression of Interlayer Atom Migration in Layered Transition-Metal Oxides
Julija Vinckeviceite, Maxwell D. Radin and Anton Van Der Ven; Materials, University of California, Santa Barbara, Santa Barbara, California, United States.

Layered transition-metal oxides continue to be an exciting area of new cathode materials. For instance, Li-excess materials appear to produce larger capacities but currently suffer from poor cyclability. Furthermore, additions of Al, Mg, and other elements into current cathodes are used to cycle batteries at higher voltages to extract more energy from the same cathode materials. In both cases, new compositions are introduced in the transition-metal layer, replacing some of the Co, Ni, or Mn. As these increasingly complex systems are (dis)charged to the extremes of their capabilities, many (not yet well understood) processes can result in battery degradation. Importantly, the layered cathode materials tend to break down when most of the active cation has been deintercalated at the end of charge, resulting in poor capacity retention and voltage fade. As Li atoms deintercalate from the layered transition-metal oxide, vacancies become available for interlayer atom migration, and atoms that leave the transition-metal layer may become stuck in the Li layer resulting in irreversible structural changes. Therefore, it is important to understand how the presence of Li, Mg, or Al in the transition-metal layer could affect (potentially irreversible) interlayer atom migration.

Using first-principles methods, we have discovered that the composition of the transition-metal host plays a very important role in facilitating interlayer atom migration. The pathway for migration includes a dumbbell with a Li ion. We analyze the energetics and electronic structure of dumbbell formation to explain why certain systems may experience more interlayer migration than others. Furthermore, we propose design principles for mitigating interlayer migration, with specific implications for NCA, Mg-doped, and Li-excess cathodes but also general insight that can be applied towards a wide range of new cathode materials. This new understanding can help in designing high energy batteries without compromising on material stability.

4:15 PM ES02.07.03

Layered lithium transition metal oxides cathodes (LiNi1-x-yMnxCo2O4) have become the cathode of choice for state-of-the-art lithium-ion batteries, which now dominate the portable energy storage market and even become the leading choice for grid storage. However, these NMC materials still achieve less than 25% of their theoretical energy density, so there is much space for improvement. Increasing the nickel content both increases the energy density and decreases the materials cost. The high nickel 622 composition is in commercial use today. The 811 composition has even higher capacity and tolerates higher materials loading and higher rates better than 622, so will become the material of choice if its increased instability can be controlled. One option to increase the capacity is to increase the charging voltage, but that leads to even higher instability. An alternative option is to reduce the 1st cycle loss, which approaches 15% of the initial capacity. We will discuss our approaches to reducing this loss, more than half of which can be recovered by reducing the discharge rate, that is the capacity is kinetically limited and by materials modification should be recovered. Part of the remainder is lost to CEI formation. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, through the Advanced Battery Materials Research Program (Battery500 Consortium).

4:30 PM ES02.07.04
Improved Manufacturing Method for Layered Nickel-Rich NMC Cathode Materials
Thomas A. Kodenkandath1, Steve Will1, Chistrel Benemlans1, Shiriram Santhanagopalan2, Xuemin Li2 and Matthew Keyser2; 1Hazen Research, Golden, Colorado, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Hazen Research, Inc., in collaboration with the National Renewable Energy Laboratory (NREL), has demonstrated a new method, in laboratory-scale experiments, of producing nickel-rich NMC cathodes. These NMC cathodes of the type Li(Ni1-x-yMnxCo2O4) (Ni >0.6) were produced using single-source inorganic-organic precursors and a process involving vertical spray pyrolysis and fluidized-bed reactions in a semicontinuous mode. The method produced amorphous phases during spray pyrolysis, which after undergoing a fluidized-bed reaction, resulted in spherical, free-flowing and nondusting soft agglomerates of well-crystallized layered nickel-rich NMC particles. The cathodes showed electrochemical performance with an initial capacity of ~200 mAh/g, a voltage stability in the range of 3.0–4.5 V, an energy density of ~800 Wh/kg, a coulombic efficiency of ~90%, and a capacity retention of approximately 70% over 100 cycles. The presentation will discuss the process, characterization, and electrochemical properties of the NMC-622 cathode powders.

SESO2.08: Poster Session
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES02.08.01
Towards Battery Chemistries Beyond Lithium-Ion Batteries—Ultrafast Sodium/Potassium-Ion Intercalation into Hierarchically Porous Thin Carbon Shells
Asif Mahmood1,2, Hassina Tabassum2 and Li Shuai1; 1Southern University of Science and Technology, Beijing, China; 2Peking University, Beijing, China.

The lithium ion batteries (LIBs) have been playing a vital role in last couple of decades to light the portable electronics due to high energy storage capability and longer cyclic life. However, the long term applications of LIBs at larger scale for automotive and other related applications face severe challenges due to lower Li abundance and higher cost. Very recently, secondary ion batteries using other metallic ions (Na+/K+) for charge storage have shown promising results in replacing traditional LIBs, owing to higher natural abundance and much lower cost. A number of electrode materials have been investigated as anode material for LIBs including carbon, ferrocyanides, phosphates, metallic nanostructures as well as metal/carbon hybrids etc. However, search for efficient electrode materials for SIBs/KIBs remains elusive.

Carbon, being the most abundant and currently commercialized anode material in LIBs, present ideal candidate for commercial SIBs/KIBs. However, the crystalline carbon structures exhibit poor insertion capability of large Na+/K+ ions (Na storage capability of 35 mAh/g in comparison to Li storage capability of 372 mAh/g) which must be addressed in order to derive highly active carbon based Na/K batteries. Although hard carbon has shown good Na+ insertion capability, however, long range order limits their full exploitation. In essence, it is imperative to present new chemistries of carbon based electrode materials which can replicate their lithium ion storage capability in sodium ion and potassium ion batteries. We have recently found that carbon materials with short order gives better insertion of large metal ions owing to relaxed interlayer spaces (~0.375 nm) in comparison to long range order where interlayer spacing is necessarily ~0.34 nm. A metal-organic framework (MOF) based methodology was used to derive hierarchically porous S and N co-doped thin carbon (S,N@C) with shell-like (average shell size ~20-30 nm, shell wall ~8-10 nm) morphology for enhanced Na+/K+ storage. Taking benefit from hollow shell-like structure and thin shell wall, the S,N@C exhibited excellent Na+/K+ storage capability without structural degradation with faster mass transport at higher discharge rates resulting in limited compromise over charge storage at high charge/discharge rate. Owing to these advantages, the S,N@C delivered high reversible capacity of 448 mAh/g at 100 mAh/g and maintain discharge capacity up to 337 mAh/g at discharge rate of 1000 mAh/g. Owing to shortened diffusion pathways, the S,N@C delivered an unprecedented value of 204 mAh/g and 169 mAh/g at discharge rate of 16000 mA/g and 32000 mA/g respectively, with excellent reversible capacity for much longer cyclic life (~4500 cycles). In addition to excellent Na+ storage capability, the S,N@C exhibited high K+ storage capability with reversible storage capability of 252.8 mAh/g at current density of 1 A/g after 80
cycles. The post-electrochemical tests revealed excellent structural stability without any visible agglomeration for rationally designed materials. The post-electrochemical RAMAN analysis revealed a slight red shift after cycling with Na+/K+ ions indicating slight expansion of carbon lattice upon reversible cycling signifying the possibility of relaxation in thin carbon lattice. The methodology clearly shows possibility of using carbon as electrode in sodium/potassium ion batteries.

Ultrafast Sodium/Potassium ion intercalation into hierarchically porous thin carbon shells, Adv. Mater., 2018, 10.1002/adma.201805430


ES02.08.02 Theoretical Lithium Perchlorate Transport Properties Calculation to Lithium-Air Battery Applications Juliane Fiates, Leandro Zanotto, Guido C. Araujo, Luís F. Franco and Gustavo Doubek; University of Campinas, Campinas, Brazil.

The world’s growing production of carbon dioxide and the desire to use more sustainable energy sources are motivating the minimization of fossil fuels employment. In this context, the development of technologies in advanced energy storage devices appears as a possibility to turn feasible the transition of engine vehicles from internal combustion to full electric motion. The lithium-ion battery which is the technology used in portable electronics has already achieved its theoretical limit (around 200 Wh/kg) [1]. Therefore, the development of novel high energy density batteries is essential to overcome limitation of the actual system. In recent years the lithium-oxygen/air battery has received great attention because of its high theoretical energy density (11686 Wh/kg), which is comparable to oil combustibles [2]. A typical lithium-oxygen battery consists of a metallic lithium anode, a porous diffusion cathode, which is commonly made of carbon composite and a catalyst, and an aprotic electrolyte which acts as a media to lithium ions transport. A full understanding of electrolyte battery element is important to find a proper composition to achieve reversibility and good capacities on charge and discharge processes. So, we are proposing in this paper the evaluation of lithium perchlorate/dimethyl sulfoxide electrolyte by molecular dynamic simulation and the calculation of transport properties such as conductivity, diffusivity and viscosity to a homogenous media. The methodology is based on building the electrolyte molecular structure and on simulating the system to evaluate transport properties. Molecular Dynamics simulation was performed with LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). PACKMOL [3] package was used to generate the ionic-electrolyte configuration. The interaction potential parameters (both intermolecular and intramolecular) were set according to the chosen force field [4, 5]. Crossed intermolecular parameters were calculated by Lorentz-Berthelot combining rules. The electrostatic interaction was computed using the Particle-Mesh scheme. For Lennard-Jones interactions, a long-range correction beyond the cutoff was applied. A step for equilibration in the canonical ensemble was carried out followed by a production stage in isothermal-isobaric ensemble. The properties were analyzed at different temperatures: 273 K, 298 K, and 313 K. The post-processing step consists on calculating transport coefficients. These coefficients will be calculated by Green-Kubo relations. The dimethyl sulfoxide density and diffusivity calculated by simulation were compared with experimental data and good agreement was observed. The electrolyte system analyses show that this approach can be used as electrolyte scanning method to evaluate feasible compounds to lithium-air batteries applications.


ES02.08.03 New Generation of Flexible Li-Ion Batteries Based on a Sheet of Carbon Nanotubes Hamda M. Alshibli1, 2, 3, Daniel Choi1, Sultan Al Dalmiani2, Prena Chatveerdi1, Amsingh Bhambh Kanagaraj1 and Maryam Al Nahyan1; Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates; United Arab Emirates space Agency, Abu Dhabi, United Arab Emirates; Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates.

Recently, the demand for thinner, lightweight design, longer life span, space effective and flexible batteries is increasing. Out of the above advantages, especially flexibility attracts scientists’ attention due to a wide range of applications and enabling variety of shapes. This study is focusing on integrating all parts of Li-ion batteries into one flexible and light sheet. We use a sheet of multi-walled carbon nanotubes, so called ‘Bucky paper’ as a matrix for cathode and anode materials while we use polymer as a solid electrolyte. Two different approaches are being implemented to assemble the batteries: First, we prepare the battery in the form of sandwich and then press the major components of the battery such as cathode, anode and solid electrolytes. We can control the load and the heating temperature of the effect. This could enhance the quality of interface among three layers. Second, low viscous polymer electrolyte is coated on anode and cathode bucky paper and press them with different loads and temperature. One challenging is to form stable interfaces between the two layers - anode/polymer electrolyte/cathode sandwich. This can be overcome by soaking the sandwich structure in the liquid electrolyte in glove box and let them to dry and using adhesive conductive binders between the sandwich to improve the interface. Integration of three major battery components (cathode, anode, solid electrolyte) is in progress.

ES02.08.04 A Universal Approach to Produce Nanostructured Binary Transition Metal Selenides as High Performance Sodium Ion Battery Anodes Zeeshan Ali1, 2, 3, and Yanglong Hou1, 2, 3; 1Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, China; 2Beijing Key Laboratory for Magnetoelectric Materials and Devices (BKLMMD), Beijing, China; 3Beijing Innovation Centre for Engineering Science and Advanced Technology (BIC-ESAT), Beijing, China.

Binary transition metal chalcogenides have recently drawn boosted attraction as anodes for sodium ion batteries (SIBs) owing to their greatly enhanced electrochemical performances. Superior intrinsic conductivity and richer redox reactions, as compared to monometal chalcogenides, are the main origins of improved performances of these binary transition metal chalcogenides. In pursuit of employing various binary transition metal selenides (B-TMSs) for energy storage, a simplistic and universal synthesis approach is highly desirable. Here, we present a facile and comprehensive strategy to produce various combinations of nanostructured B-TMSs by the use of either nitrates or sulfates of corresponding metals in a high yield room temperature solution reaction. Furthermore, the structure evolution mechanism of nano rods from precursor nanosheets was investigated through the study of products obtained after various reaction durations. As proof of concept, high surface area and hierarchical nanosheets of Fe2NiSe2, Fe2CoSe2 and NiCoSe2 (termed as FNSe, FCSe and NCSe respectively) were manufactured and employed as anodes for sodium ion batteries. These as prepared anodes of B-TMSs exhibited adequately high energy capacities (e.g. 755, 660 and 397 mA h g−1 after 100 cycles at 1 A g−1 for FNSe, FCSe and NCSe, respectively) and excellent rate capabilities (e.g. 776 mA h g−1 at 0.5 A g−1 and 432 mA h g−1 at 20 A g−1 for FNSe, 655 mA h g−1 at 0.5 A g−1 and 466 mA h g−1 at 20 A g−1 for FCSe and then 660 mA h g−1 at 0.5 A g−1 and 366 mA h g−1 at 20 A g−1 for NCSe). In addition to this, FNSe and FCSe also presented extraordinary stable life of 2500 cycles (with reversible capacities of 554.2 and 554.6 mA h g−1 at 4 A g−1, respectively). In situ X-ray X-ray diffraction analysis combined with ex situ X-ray and selected area diffraction analysis revealed that the electrodes of FNSe, reversibly transform into the discharge product (Na2Se) through multistep reaction with sodium ions. When employed in sodium full batteries with lab-made Na0.5V2(P04)3/C cathode, as prepared B-TMSs anodes presented reasonably high reversible specific capacities (228.5, 216.5 and 100.2 mA h g−1 at 0.1 A g−1 after 100 cycles for FNSe, FCSe and NCSe, respectively). Overall, the presented strategy will pave the way for the development of numerous binary transition metal chalcogenides which are the potential materials for energy storage and conversion systems.
A Cost Effective Route to Synthesize LiFePO₄ in a Quasi-Open Environment Assisted by Starch as an Oxidation Protective Component

Fei Gu, Kichang Jung, and Alfredo A. Martinez-Morales

Materials Science and Engineering, University of California, Riverside, Riverside, California, United States; Chemical Engineering, University of California, Riverside, Riverside, California, United States.

The development of Li-ion cathode materials is moving forward to a new era. Lithium iron phosphate (LiFePO₄, LFP) is widely used by the battery industry and it has the potential to continue playing an important role in the future. Mainly driving by a stable operating voltage (3.5 V vs. Li/Li⁺) and a high theoretical capacity (170 mAh/g). Additionally, LFP has excellent cycling performance, high safety, environmental friendliness, and low raw material cost. To further increase the competitiveness of LFP by decreasing production cost, an approach to synthesize LFP with coated carbon (LFP/C), via lithiation in a quasi-open air environment is investigated in this work. In contrast to the generic solid state synthesis for LFP, our approach is more time efficient with the lithiation process completing under 30 minutes. Furthermore, our approach is a cost-effective process since the reaction is conducted under atmospheric pressure in a quasi-open environment. Starch is used as a carbon source during synthesis, providing a reducing environment to protect the synthesized LFP from oxidation, while forming a carbon coating on the surface of LFP. The carbon coating enhances the electrochemical performance of the assembled Li-ion batteries by improving electric conductivity of the LFP cathode. The combination of LFP synthesis process and LFP carbon coating process in one step further improve the efficiency of our quasi-open synthesis approach.

Starch is selected as carbon source because it has a high carbon content that produces LFP/C with a high efficient coating, at a low fabrication cost. This work investigates the effect of the amount of starch added, reaction temperature, and reaction time for LFP synthesis. Several techniques are used to characterize the properties of synthesized LFP/C. The crystal structure and chemical composition of the synthesized material are characterized by X-ray Diffraction (XRD) and Energy Dispersive Spectroscopy (EDS). The grain size of resulting materials is determined by Scanning Electron Microscopy (SEM). The degree of carbonization is characterized by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). The electrochemical performance of synthesized cathode is investigated by Cyclic Voltammetry (CV) and the performance of assembled batteries is tested via an Arbin Tester. The mechanism of starch assisted LFP synthesis and the decomposition process of starch are investigated. These reaction processes are studied by Differential Scanning Calorimetry and Differential Thermal Analysis (DSC and TGA, respectively).

Electrochemical Intercalation of 2D Graphene with FeCl₃

Kai L. Kuntz, Carolyn Chen and Scott Warren; University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Intercalation—the insertion of guest species into the interlayer space of a layered host material—is a platform to drastically alter properties. By inserting either an electron donor or acceptor species into a material, the fermi energy of the host shifts, resulting in different electronic and optical properties. While layered materials have been intercalated since 1841, their two-dimensional (2D) counterparts have only recently been intercalated with the first demonstration in 2009. As the host dimensions are reduced, the energetic penalty for intercalation, and therefore the rate and mechanism, are altered. Furthermore, since 2D materials are known to exhibit different electronic and optical properties than bulk, intercalation offers a unique platform to further alter and tune the properties of thin material.

Iron trichloride (FeCl₃) intercalates both bulk and few-layer graphite, resulting in a hole-doped graphite host, with the stage determining the extent of doping. In a stage I intercalation compound, each host layer is adjacent to an interlayer carbon, while in lower stages, the stage number dictates the number of host layers between intercalant layers. Ultimately, the carrier concentration and resulting properties of the compound are dependent on the stage of intercalation.

FeCl₃ has been previously intercalated in bulk and few-layer graphite thermally, and in bulk graphite electrochemically in water (Carbon N. Y. 3(5), 285-290 (1997)) or propylene carbonate (Carbon N. Y. 36, 383-390 (1998)). Thermal methods produced stage I FeCl₃-graphite, while electrochemical methods yielded stage II in the bulk material. We hypothesize that reducing the dimensions of the graphite host will reduce energetic barriers and allow for stage I compounds to be produced electrochemically. Furthermore, we hypothesize that FeCl₃ might be able to be deintercalated from few-layer graphite, enabling this compound to be studied for reversible optoelectronic applications.

Here, we electrochemically intercalate bulk and few-layer graphite with 10M FeCl₃ in propylene carbonate under inert environments (< 1 ppm O₂, < 0.1 ppm H₂O). We monitor the intercalation through in-situ techniques, including cyclic voltammetry, optical microscopy, and Raman-spectroscopy, as well as ex-situ techniques, including X-ray photoemission spectroscopy (XPS). Characterization of the resulting compound via XPS indicate the presence of FeCl₃ in the interlayer space. Raman spectroscopy further supports the electrochemical intercalation of bulk and few-layer material, resulting in a hole-doped host. Interestingly, we find that the thin material results in mixed stage I and stage II compounds, verifying our initial hypothesis that reduced dimensions enable access to higher stages and carrier concentrations, which was unattainable in bulk material by electrochemical methods. Furthermore, we investigate the reversibility of this intercalation through calculations and experiments. Calculations using density functional theory indicate that this intercalation should be reversible. We use in-situ characterization techniques to investigate this experimentally.

In this work, we employ in-situ and ex-situ techniques to demonstrate the first electrochemical intercalation of few-layer graphite with FeCl₃, allowing the role of dimensions in the intercalation to be investigated. Furthermore, this work is the first to demonstrate stage I FeCl₃-graphite through electrochemical techniques. Finally, we address the reversibility of this system and its promise for reversible optoelectronic technologies, including optical switches and batteries.

Three-Dimensional Hierarchical LiNi₀.5Mn₁.₅O₄ Desert-Waves—Topography-Inspired Conductive Network for Lithium-Ion Batteries with High-Rate Capability

Tao Mei and Xianbao Wang; Hubei University, Wuhan, China.

Inspired by the topography of desert, three-dimensional (3D) hierarchical LiNi₀.5Mn₁.₅O₄ desert-waves (LNMO-DW) composed of primary two-dimensional (2D) nanodiscs is ingeniously synthesized via a template-free route. Its formation can be attributed to the synergic effect of hydrate hydrate (HH) and ethylene glycol (EG) during the hydrothermal process. The as-obtained 3D hierarchical LNMO-DW triggers fast electrode kinetics and abundant electroactive zones by enabling multi-directional efficient transmissions for both lithium ions and electrons. The rate capability and cycling stability of LNMO-DW are improved to a superior level compared with the control groups and other reported works, which proves that 3D hierarchical desert-waves-like structure is one of the optimal structures for LNMO. Its specific capacity reaches 130 mAh/g at 10 C after 200 cycles, together with capacity retention of 91%. Noticeably, even when cycling at the high rates of 15 and 20 C after 200 cycles, the discharge capacities are still up to 117 and 108 mAh/g, respectively. The corresponding structural formation mechanisms and electrochemical principles have also been unravelled.

Tunnel Intergrowth Structures in Manganese Dioxide and Their Influence on Ion Storage

Yifei Yuan, Bryan Bylbes, Cong Liu, Jun Lu, Khalil Amin, Ekaterina Pomerantseva and Reza Shahbazian-Yassar; 1University of Illinois at Chicago, Chicago, Illinois, United States; 2Drexel University, Philadelphia, Pennsylvania, United States; 3Argonne National Laboratory, Argonne, Illinois, United States.

Controlled synthesis of homogeneous tunnel-structured materials has been a grand challenge due to the lack of understanding on heterogeneities associated with tunnel structuring and abnormalities. The presence of tunnel structure heterogeneity disables the quantification and optimization of the performance of various tunnel-structured functional materials in their targeted applications such as catalysis, water purification, energy storage, and sensing. Manganese dioxide (MnO₂) is a highly polymorphic material with several well-known tunnel-structured phases such as β-MnO₂, α-MnO₃, and T-MnO₃ featuring 1×1 tunnels, 2×2 tunnels, and 3×3 tunnels, respectively. For over a century, the tunnel-dependent properties of MnO₂ in areas such as catalysis and ion transport have been gradually realized, and numerous studies have been devoted to the synthesis of homogeneous tunnel phases. Until recently, the structural details of the tunnel phases have not been revealed clearly, especially down to the atomic level.

Here, we demonstrate for the first time the correlation between homogeneity of the tunnels and their dimensions. Utilizing state-of-the-art aberration-corrected scanning transmission electron microscopy that is sensitive to local structure information, we found that while β-MnO₂ possesses a homogeneous 1×1 tunnel phase, the tunnel homogeneity decreases when tunnel dimension increasing from 2×2 tunnel-structured α-MnO₃ to 3×3 tunnel-structured T-MnO₃. For α-MnO₃, a complicated 2×3 and 2×4 tunnel intergrowth as
well as tunnel shift (~7 Å) and rotation (~90°) with smaller 1×2 tunnels accommodating the structure mismatch are disclosed. For T-MnO$_2$, a larger density of defective tunnel intergrowths is observed. The existence of large tunnels (~10 Å) such as 3×4, 3×5, 3×6, 4×4, 4×6, 5×3, 5×4, and 5×5 tunnels is discovered in this work for the first time. Such tunnels are found to be stable within the 3×3 tunnel-dominated T-MnO$_2$ matrix. The complicated tunnel intergrowths discovered in this work are shown to affect the ion storage behavior in the tunnel-structured materials as revealed by in situ TEM of a single MnO$_2$ nanowire exhibiting such tunnel heterogeneity. The findings of this work call for renewed attention to the synthesis of homogeneous tunnel-specific MnO$_2$ phases for applications where tunnel homogeneity is desired.

**ES02.08.09 Sodium Ion Conduction in Germanium Phosphide and Germanium Arsenide**
Migdad Razzaq$^{1}$, Shunda Chen$^{1}$, Sahyasaachi Sen$^{1}$, Kirill Kovnin$^{2}$ and Davide Donadio$^{3,4}$; $^{1}$University of California, Davis, Davis, California, United States; $^{2}$Iowa State University, Ames, Iowa, United States.

For decades, the state-of-the-art has been lithium-ion batteries (LIB). But, with the growing need for energy storage and applications, new battery materials have to be studied. This would allow to replace lithium with more abundant and safer elements like sodium.

Here we use first-principles calculations to study the intercalation of sodium in two germanium-based layered materials: germanium phosphide (GeP) and germanium arsenide (GeAs), which are promising candidates for applications in sodium-ion batteries. Both GeP and GeAs have a Gallium Telluride-like layered monoclinic crystal structure. The interlayer van der Waals (vdW) gap provides promising sites for metal ion intercalation and diffusion. Our calculations, performed in the framework of density functional theory with an accurate non-local vdW functional, show a rich phenomenology. Sodium adsorption becomes exothermic beyond a threshold concentration and causes significant rearrangements of the crystal structure, accompanied by semiconductor/metal/semiconductor transitions. Nodged elastic band calculations, in addition to molecular dynamics, are used to study the diffusion path of the sodium ions.

**ES02.08.10 An Innovative Metal-Sulfide Cathode Active Material for Aluminum-Ion Batteries**
Yuxiang Hu; Chemical Engineering, The University of Queensland, Brisbane, Queensland, Australia.

Rechargeable aluminum-ion batteries (AIBs) are attractive next generation energy storage devices due to its low cost, high specific capacities, and good safety.$^{[1]}$ However, the lack of suitable electrode materials with high capacity and enhanced rate performance makes it difficult for real applications. Herein, we report the preparation of three dimensional (3D) reduced graphene oxide (RGO)-supported SnS$_2$ nanosheets hybrid and its enhanced electrochemical performance as a novel electrode for AIBs. A to-date one of the highest capacities of 392 mAh g$^{-1}$ at 100 mAh g$^{-1}$ and good cycling stability is achieved in the resultant new material. The 3D reduced graphene oxide-based network and nano-size active material endow the composite high electronic conductivity and fast kinetic diffusion, which contributes to the high cycling performance (112 mAh g$^{-1}$ at 1000 mAh g$^{-1}$). Furthermore, our detailed characterization also verifies the intercalation and de-intercalation of the aluminum anions into the layered SnS$_2$ nanosheets during the charge-discharge process.$^{[2]}$

References

**ES02.08.11 Nitrogen-Filling into Oxygen Vacancy Enable the Enhanced Fast Lithium-Ion Storage**
Yanglansen Cui$^{1}$, Nicholas Bedford$^{1,2}$, Rose Arnal$^{1}$ and Da-Wei Wang$^{1}$; $^{1}$School of Chemical Engineering, The University of New South Wales, Sydney, New South Wales, Australia; $^{2}$X-ray Sciences Division, Argonne National Laboratory, Argonne, Illinois, United States.

Although the transitional metal oxide (TMO) has been intensively investigated as the promising candidate for lithium-ion storage due to their high theoretical specific capacity, the poor conductivity and sluggish of solid ion diffusion rate still hinder their rate capability. Herein, the nitrogen doped amorphous tungsten oxide (N-WO$_3$) is fabricated and further used as electrode material for lithium-ion storage. Besides, the atomic structure of the obtained N-WO$_3$ is investigated by X-ray absorption spectrum (XAS) including XANES and EXAFS-FIT, suggesting that the tungsten center in N-WO$_3$ is not only coordinated with oxygen atom but also the nitrogen atom. Impressively, the as-prepared N-WO$_3$ exhibits an ultrastatic storage capability of 315 mAh g$^{-1}$ even at a high current density of 10 A g$^{-1}$ with only 5% decay of capacity after 4000 cycles which is superior to that of most reported WO$_3$-based electrodes. The coordinated N in N-WO$_3$ facilitate both the charge transfer and solid-state lithium ion diffusion rate, leading to the rate capability enhanced. The methodology proposed in this work will point out a way to design TMO-based electrode materials on large-scale.

**ES02.08.12 Tin Phosphide Based Materials with Low Irreversible Capacity as Anode for Sodium-Ion Batteries and Capacitors**
Francois Beguin and Agnieszka Chojnacka; Poznan University of Technology, Poznan, Poland.

Nowadays, owing to the low cost and abundance of sodium resources, Na-ion batteries (NiBs) and Na-ion capacitors (NiCs) attract a lot of research attention. However, the optimization of the Na-ion technology requires urgently the development of stable anode materials with high reversible capacity, low irreversible capacity and appropriate potential window. Tin based materials form rich alloys with sodium, yielding much higher theoretical capacity (from 847 mAh g$^{-1}$ for Sn to 1132 mAh g$^{-1}$ for SnP$_3$) than carbon-based materials. Despite the very large reversible capacity ($C_{\text{irr}}$) displayed by SnP$_3$, its relatively high $C_{\text{irr}}/C_{\text{cap}}$ ratio ($C_{\text{irr}}$ irreversible capacity) makes it inappropriate for practical application. In this context, we disclose a simple and inexpensive method to obtain SnP$_3$-based electrode materials showing low irreversible capacity and excellent cycle life, allowing them to be employed as negative electrode for electrochemical energy storage systems.

SnP$_3$ was formed by facile high-energy ball milling in Ar atmosphere, and it was then mixed with hard carbon (HC) in the mass ratio 1:1 by ball milling. The electrochemical properties of SnP$_3$ and HC/SnP$_3$ electrodes were determined by cyclic voltammetry (CV) and galvanostatic charge with potential limitation (GCPL) using Na as counter/reference electrode and 1 mol L$^{-1}$ Na$_2$CO$_3$ in a 1:1 mixture of ethylene carbonate (EC) and propylene carbonate. The HC/SnP$_3$ and HC/SnP$_3$-based electrodes display a very low irreversible capacity, ca 60 mAh g$^{-1}$ and 83 mAh g$^{-1}$, respectively. In addition, the HC/SnP$_3$-based electrode exhibits low ohmic drop of 13 mV, as compared to 30 mV for SnP$_3$. Electrochemical dilatometry during sodium insertion (potential range from 2 V to 0.1 V vs Na/Na$^+$) in SnP$_3$ and HC/SnP$_3$-based electrodes with same mass of SnP$_3$ demonstrated volume change of 70% and 50%, respectively, revealing that hard carbon acts as a buffer for SnP$_3$. The viability of presodiated SnP$_3$ and HC/SnP$_3$-based anodes in a full electrochemical cell has been demonstrated in Na-ion capacitors (NiCs) with activated carbon (AC) positive electrode, and using 1 mol L$^{-1}$ Na$_2$CO$_3$ in a EC/PC electrolyte. Both NiCs systems demonstrated an energy density ca. 45 Wh kg$^{-1}$ at a current density of 0.5 A g$^{-1}$ in the cell potential range 2.2 V - 3.8 V. After 4500 cycles at 0.5 A g$^{-1}$, an excellent capacitance retention of 97% was observed for the NiC with HC/SnP$_3$ electrode, demonstrating that these materials are promising anodes for a new generation of NiCs and NiBs.

**ES02.08.13 Effect of Porosities and Surface Morphologies in Si Anode for Lithium Ion Batteries using Magnesiothermic Reduction**
Jiamei Liu$^{1}$; Changling Li$^{1}$, Bo Dong$^{1}$, Yiran Yan$^{2}$, Ruoxu Shang$^{3}$, Cengui S. Ozkan$^{1,3}$ and Mihrimah Ozkan$^{1,3}$; $^{1}$Electrical Engineering, University of California, Riverside, Riverside, California, United States; $^{2}$Material Science and Engineering, University of California, Riverside, Riverside, California, United States; $^{3}$Mechanical Engineering, University of California, Riverside, Riverside, California, United States.

Si, with its high theoretical capacity (3572 mAh g$^{-1}$), high energy density and low self-discharge rate, is considered as the most promising anode material for next generation lithium ion batteries (LIBs). Recently, we published a ultra-fast Mg-thermal-reduction method for the production of scalable coral-like Si powders with a high surface area and...
three-dimensionally (3D) interconnected structures. In this work, we obtained Si materials with different porosities and surface morphologies via controlling over magnetostructural reduction. The porosities, surface morphologies, and phase purities of the synthesized nano-Si powders were analyzed by BET analysis, SEM, TEM, XRD, and Raman spectroscopy. Furthermore, electrical characteristics of different Si electrodes were examined by electrochemical impedance spectroscopy (EIS), cyclic voltammetry, and galvanostatic charge-discharge test. The Si electrodes exhibited long cycling stabilities, good rate capabilities, and high reversible capacities. We proved that the cycling performance and stabilities of these Si anodes significantly depend on the conditions of magnetostructural reduction.

ES02.08.14
Sodium Intercalation in TiO2 Electrodes During Dis-Charging of Sodium-Ion Batteries Monitored by Operando XANES Measurements
Andreas Siebert1, Xinwei Dou2, Roberto Félix1, Evelyn Handick1, Raul G. Dzie1, Regan Wilks1, Daniel Buchholz2, Giorgia Greco3, Stefano Passerini1 and Marcus Bar1,4,5, Helmholtz-Zentrum Berlin, Berlin, Germany; 2Helmholtz Institut Ulm, Ulm, Germany; 3Forschungszentrum Jülich GmbH, Erlangen, Germany; 4Energy Materials In-Situ Laboratory Berlin (EMIL), Berlin, Germany.

Lithium ion batteries (LIBs) are currently one of the preferred technologies to store electrical energy. However, the worldwide availability of Li is limited, and it is questionable whether the rising energy storage demands can be fulfilled by LIBs in the future [1]. Sodium ion battery (SIB) technology could provide an alternative, as Na is readily available, cheap, and environmentally friendly. SIBs additionally allow AI to be used as a new collector instead of Cu, which is heavier and more expensive. Recently, the excellent performance of a SIB anode based on TiO2 nanoparticles has been demonstrated [2,3]. In contrast to the well-optimized electrochemical behavior of state-of-the-art anodes, however, there is still a lack of understanding of the mechanisms involved in the performance of these nanoparticle anodes. In particular, it is challenging to unravel the structural and electronic changes of the anatase TiO2 nanoparticles and the loss of crystallinity of the anodic nanomaterial upon Na uptake. For instance, it has been shown that initial sodiation leads to an irreversible capacity loss of nearly 40% [3].

X-ray absorption near edge spectroscopy (XANES) of the Ti K-edge is ideal for studying the electronic and geometrical structure around the probed Ti atom and its nearest neighbors and, hence, can reveal effects of sodium intercalation. However, ex situ experiments performed on disassembled electrodes can raise questions about the relevance of the results due to the expected changes of the electrode material due to air exposure, sample transport, and preparation. To gain direct, relevant insights into the intercalation process of Na into the TiO2 nanoparticle anode material, we designed an operando XANES experiment using a modified coin cell equipped with an X-ray transparent Kapton® window and a 6 μm-thick Al foil current collector. This setup allowed the measurement of the Ti K-edge (at the HZB BESSY II synchrotron source in the HiKe endstation [4] at the KMC-1 beamline) of the TiO2 electrode while cycling the coin cell battery, i.e. desodating the electrode.

The Ti K absorption edge reveals the average Ti oxidation state of the TiO2 anode material, which changes during the sodiation from the expected +4 (Ti4+) oxidation state in the original anatase structure to values below +3. The operando results of the Ti K-edge show, that the oxidation state increases during the desodiation but does not reach Ti4+ again due to the presence of irreversibly intercalated sodium. The study is also focused on the evolution of the pre-edge structure of the Ti K-edge during the descharging. In the initial sodiation cycle, the pre-peak changes from the characteristic four-peak feature related to anatase [5] to a structure dominated by a single peak, hinting at a change in the number of nearest neighbors around the probed Ti atoms (from six to five or even four neighbors) [6]. The single peak intensity increases during the first desodiation, suggesting that the anode material does not completely recover the original anatase structure after the first full descharging cycle. The subsequent cycling shows the same spectroscopic trend on the pre-edge feature, revealing a stable intercalation process after the irreversible structural rearrangement of the TiO2 during the first sodiation process.


ES02.08.15
Intermetallic Clathrates as Insertion Anodes for Li-Ion Batteries
Andrew M. Dopilka1, Ran Zhao1, Jon M. Weller1, Svilen Bovev2, Xihong Peng2 and Candace K. Chan1; 1Material Science and Engineering, School of Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, Arizona, United States; 2Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States; 3College of Integrative Sciences and Arts, Arizona State University, Mesa, Arizona, United States; 4School of Molecular Sciences, Arizona State University Tempe, Arizona, United States.

Stable intercalation anodes for Li-ion batteries are generally comprised of two groups: graphite and Ti/Nb oxides. Graphite electrodes are reversible but can’t be operated at high current rates because of particle fracture and dendrite formation as a result of volume expansion and a low reaction potential (0.1 V). Li2TiO3 is a popular insertion anode that demonstrates good stability (zero strain) and fast charging but its high reaction voltage (1.55 V) lowers the energy density of the full cell. A crystal framework that allows low strain Li-insertion at a lower potential (i.e. 0.5 -1.0 V) could allow for fast charging with less propensity for dendrite formation while also increasing the energy density of the cell. Intermetallic compounds tend to have reaction voltages with Li between 0.2 V – 1.0 V, which makes them interesting candidates for insertion anodes. However, Li alloying accompanied by a large volume expansion is common in these materials (e.g. Si, Ge, Sn) so host frameworks that allow bulk Li insertion into the structure before a Li alloying reaction are needed. Intermetallic clathrates are crystal structures that are comprised of a group IV framework of cages which host alkali guest atoms in the center of the cages (e.g. Ba46Si44, K4Ge44). This structure type has led to many interesting materials properties such as thermoelectricity, superconductivity, hydrogen storage, and tunable optical properties. Recently, our group has been studying the electrochemical reactions of clathrates with Li to understand how the defects of clathrates affect the electrochemical properties and if reversible Li insertion into the crystal structure is possible.

Our recent results investigating the Ba46Al44Si44 and Ba46Al44Ge44 Type I clathrate systems will be summarized1,2. Interestingly, the Si clathrates do not undergo amorphization reactions typical of intermetallic compounds, indicating that the structure is stable in the potential range for anodes. The Ge clathrates, however, do undergo amorphization reactions to form Li-rich amorphous phases. From density functional theory calculations, X-ray diffraction, and electrochemical impedance spectroscopy, Li insertion into the cage structure seems unlikely. We find that the Ba inside the cage frustrates Li mobility and that bulk diffusion in the cage structure would require guest atom vacancies.

Next, the synthesis and electrochemical characterization of empty type II Si clathrates (Si84) would be reported. Previous work has proven with nuclear magnetic resonance (NMR) that Li can be inserted into the empty clathrate cages of Si84. This manifests as a potential plateau at (300 mV) prior to the amorphization of the Si lattice. This is distinctly different from diamond structured Si which only shows the typical two-phase amorphization reaction plateau. Initial results suggest that reversible Li insertion in Si84 is possible by applying a voltage cutoff before the amorphization reaction. We aim to understand the pathways, reversibility, and kinetics of Li insertion in the empty type II Si framework and evaluate them as Li insertion anodes. Since the Li insertion voltage is 300 mV for Si84, the risk of dendrite formation at higher current rates could be reduced while maintaining higher energy density cell due to a low reaction voltage. These results would be interesting for the future design of anodes that have a lower reaction voltage than the Ti/Nb oxides but still demonstrate rapid, reversible Li insertion.


ES02.08.16
Intercalation Energy Barrier Tuning of MoS2 for Aqueous Zinc Ion Storage
Hanfeng Liang; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Aqueous Zn-ion batteries present a low cost, safe, and high-energy battery technology, but suffer from the lack of suitable cathode materials because of the sluggish intercalation kinetics associated with the large size of zinc hydrate. Herein we report an effective and general strategy to transform inactive intercalation hosts into efficient Zn2+ storage materials through intercalation energy barrier tuning. Using MoS2 as a model study, we show both experimentally and theoretically that even hosts with originally poor
Herein, we report that high-energy ball milling (HEBM), which is widely employed in battery research to optimize electrochemical performance of active materials through particle size reduction, is not suitable for VOPO$_4$. Our results reveal that structural distortions and defects introduced in the material during HEBM impede the kinetics of high-lattice formed by the de-intercalation of K from KVOPO$_3$. The synthesis and characterization of these materials were described, together with future opportunities. This work was supported by the DOE–EPRC–NECCES.

Layered Vanadium Oxides as a High Energy Cathode Material for Nonaqueous Magnesium-Ion Batteries

M. Stanley Whittingham, Carrie Siu, Jia Ding and NorthEast Center for Chemical Energy Storage (NECCES) Team; State University of New York at Binghamton, Binghamton, New York, United States.

We have shown that it is possible to reversibly intercalate two lithium or sodium ions into phosphate host lattices without any degradation of the host lattice. Such reactions are highly dependent on the host lattice. We have shown that two lithium ions can intercalate into the e- and b-VOPO$_4$ phases. In these lattices, the first lithium ion intercalates by a slow two-phase reaction VOPO$_4$+LiVOPO$_4$, whereas the second ion intercalates by a fast single-phase reaction, Li$_{1+x}$VOPO$_4$. However, for the larger sodium ion, the expanded lattice formed by the de-intercalation of K from KVOPO$_4$ is required for the intercalation of two sodium ions. The synthesis and characterization of these materials will be described, together with future opportunities. This work was supported by the DOE–EPRC–NECCES.

References:


Tetrahedral polyoxovanadium compounds make up a large family of intercalation cathodes for lithium cathode and solid electrolytes pursuing in next generation lithium batteries. While cathode and solid electrolytes have different requirements on electronic conductivity, high lithium ionic conductivity is of common significance to both electrode materials for high energy density and stable solid state electrolytes for better safety. However, designing a fast ionic transport in tetrahedral polyoxovanadium oxides requires detailed understanding of the interplay of geometric coordination with electronic band structures. This work presents a rational design of high capacity cathode, which utilizes V-doping to simultaneously engineer electronic conductivity and lithium transport in tetrahedral framework silicate, Li$_2$CoSiO$_4$(LCSO). First-principles modeling, in coupling with electrostatic field analysis by Madelung matrix, reveals a profound structural characters of delithiated Li$_2$CoSiO$_4$ (x = 2, 1, 0). However, the calculation indicates that V-doping not only introduces significant gap states that modify both electronic conductivity and redox activity of Li$_2$CoSiO$_4$, but also significantly alter the lithium transportation, which predicts a 0.20 eV lower of the transition barrier. The calculated diffusion coefficient shows that V-doping enhances on transport by three orders of magnitude. A series of Li$_2$Co$_{1-x}$Si$_x$O$_4$ (x = 0.00, 0.05, 0.10, 0.12, 0.16, 0.20) samples have been synthesized to verify and validate the first-principles prediction, combining with characterization by XRD, SEM and Raman spectroscopy studies. Electrochemical testing shows that carbon coating LCSO with 10% V substituted Si delivers an initial discharge capacity of 220.1 mAh g$^{-1}$ with 74% coulombic efficiency and impressive cycling stability. This study may provide a new venue for high performance design of all-solid-state lithium secondary batteries from...
Earth-abundant spinel ferrites are potential low-cost negative electrodes for rechargeable Li-ion batteries because they can undergo reversible conversion reactions upon deep discharge. But iron oxides can also function as positive electrodes provided that a sufficient number of cation lattice vacancies and proton-stabilized oxygen sites are present and accessible for reversible Li+ or Na+ insertion. The challenge is to create these lattice sites in an otherwise vacancy-deficient oxide. We address this challenge and achieve technology-relevant cation–insertion capacities by generating cation lattice vacancies using design strategies that significantly increase the defect nature of the spinel. First, we produce spinel ferrites in aerogel forms (materials with high surface area and through-connected mesoporosity), thus amplifying the surface-to-bulk ratio and providing facile access to vacancies at the inherently disordered surfaces. We then make the oxide highly defective with mild heat treatment in an O2-rich atmosphere that removes synthesis precursors while avoiding crystallization. The defect nature of the spinel is further amplified by substituting a third of the iron sites with high-valent vanadium (V4+ and V5+). We find that choosing thermal treatments that predominantly result in ferrites substituted with V4+ delivers the largest Li+ and Na+ insertion capacities, approaching 130 mAh g−1 and 70 mA h g−1, respectively. We also report on doping the vanadium sites with aluminum (~5%) to improve cycling stability when these spinel ferrites are used as positive electrodes for Li+ insertion.

10:00 AM BREAK

Wenxiang Chen, Xun Zhan, Binbin Luo, Zihao Ou, Hong Yang, Jian-Min Zuo and Qian Chen; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

We study the electrochemical and chemo-mechanical responses of nanoparticles of different sizes as cathode materials in magnesium ion batteries. Distinctive structural phase transition pathways are observed in nanoparticles of different sizes in the Mg ion intercalation as characterized by X-ray diffraction analysis. Small nanoparticles exhibit a single-phase transition while heterogeneous phase evolution is observed in big nanoparticles. Further examination at nanoscale by nano-beam diffraction and energy-dispersive X-ray spectroscopy reveals that the difference in the phase evolutions could be attributed to the short diffusion length and single crystallinity in the small nanoparticles. Our work shows that engineering the nanoparticle size and crystallinity has a direct influence on Mg ion intercalation processes, which rationally guides the design of electrodes with high capacity and high stability.

11:15 AM ES02.10.03

In Silico Investigation of Electrode Materials for Rechargeable Magnesium Batteries Nikhil Medhekar, Mingchao Wang, Jodie Yuwono and Nick Birbilis; Monash University, Clayton, Victoria, Australia.

Rechargeable Mg-ion batteries (MIBs) are rapidly emerging as a plausible alternative to Li-ion batteries (LIBs) in terms of energy density, scalability and operation safety. However, key challenges in addressing the electrochemical stability and cyclability of potential electrodes, such as Mg metal as anode and layered transition-metal dichalcogenides (TMD) as cathode, pose questions regarding their feasibility as electrodes in MIBs. The inadequate understanding of reaction mechanisms during (de)magnesiation process hinders the practical application and optimal design of electrode materials. Here we carry out first-principles calculations to investigate the electrochemical behavior of Mg metal and Group 14 as anodes, as well as layered TMD as cathodes. We find that unexpected self-catalytic behavior of Mg induced by surface hydroxylation can be effectively controlled by impurity enrichment (alloying with Group 14 and 15 elements) and surface oxidation. To replace Mg by Group 14 elements as MIB anodes, comprehensive kinetic and thermodynamic investigations reveal that amorphous Ge and crystalline Sn can work as potentially effective anode materials in Mg-ion batteries. We also find out that a small overpotential is necessary for avoiding aggregation of Mg at anode/electrolyte interfaces during Mg-X reactions. In addition to anodes, our studies demonstrate that the expansion of layer spacing in TMDs (i.e. TiS2 and MoS2) enables faster intercalation and diffusion of MgCl2 species in TMD interlayers owing to the low energy barrier, and further enhancing the theoretical energy capacity of Mg-TMD.

SESSION ES02.11: Multivalent Intercalation—Zn and Beyond

Session Chairs: Benjamin Morgan and Kimberly See

Thursday Afternoon, April 25, 2019

PCC North, 100 Level, Room 126 C

1:30 PM ES02.11.01

Multi-Electron Cathodes for High-Capacity Alkali-Ion Batteries Shyue Ping Ong1, Yuh-chieh Lin1, Marc Hidalgo2, Antonin Grenier1, Natalya Chemova2, Louis F. Piper3, Karena Chapman1 and M. Stanley Whittingham1; 1University of California, San Diego, La Jolla, California, United States; 2Binghamton University, The State University of New York, Binghamton, New York, United States; 3X-ray Division, Argonne National Laboratory, Lemont, Illinois, United States.

Multi-electron cathodes, which utilizes more than one redox couple per transition metal, are a path towards higher capacities and energy densities. In this talk, I will discuss the efforts of the NorthEast Center for Chemical Energy Storage, a DOE Energy Frontier Research Center, in developing multi-electron cathodes for both Li and Na intercalation utilizing the V3+/4+ and V4+/5+ redox couples. I will demonstrate how the integrated application of density functional theory calculations, in operando characterization and
electrochemical measurements has provided deep insights into the relative phase stability and electrochemical performance of the \( \text{e} \), \( \text{f} \) and \( \text{g} \)-polymorphs of VOPO\(_4\), and led to optimized cathodes achieving close to full two electron cycling. Furthermore, we have synthesized all three polymorphs starting from a single precursor – LiVOPO\(_4\)H\(_2\)O – through careful control of the \( \text{O}_2 \) environment and temperature. Finally, I will also highlight our exploration of other VOPO\(_4\) phases with larger alkali ions, e.g., KVOPO\(_4\), for improved Na cycling.

2:00 PM ES02.11.02
High Capacity and Stable Cyclic Performance of 2D MXene Cathodes for Rechargeable Aluminum Batteries
Armin VahidMohammadi and Majid Beidaghi; Auburn University, Auburn, Alabama, United States.

The emerging market of electric vehicles (EVs) has raised the bar for development of safer rechargeable batteries with significantly higher energy densities. Even though currently lithium-ion (Li-ion) batteries are the dominant battery technology for portable electronics and EVs; the scarcity of lithium resources, its high cost of extraction from brines, and safety issues arising from their flammability have further increased the need for batteries beyond Li-ion technologies. Among various battery technologies, multivalent-ion batteries that store and deliver charge by intercalation of divalent (Mg\(^2+\), Ca\(^2+\), Zn\(^2+\)) or trivalent (Al\(^3+\)) ions into layered host materials are of interest as they can potentially deliver higher energy densities at a reduced cost compared to Li-ion batteries. Particularly, rechargeable aluminum batteries that utilize aluminum metal as the anode are considered as one of the most promising alternative energy storage systems for current battery technologies because aluminum is the most abundant metal in Earth’s crust, offers three-electron redox reactions in electrochemical systems, and can be handled in the open air leading to higher safety and facile cell fabrication. Also, it has the highest theoretical volumetric capacity of 8040 mAh cm\(^{-2}\) among all metals and a reasonably high theoretical gravimetric capacity of 2980 mAh g\(^{-1}\). Recently, we reported on rechargeable aluminum batteries utilizing two-dimensional (2D) \( \text{V}_\text{2} \text{C} \) MXenes as intercalation-type cathodes delivering exceptional capacities and rate-capability. \(^1\) MXenes are a family of 2D transition metal carbides and nitrides with a general formula of \( \text{M}_X \text{C}(\text{M} \text{is a transition metal, } X \text{is carbon and/or nitrogen, } n=1,2, \text{ and } 3, \text{ and } T \text{ represents different surface functional groups}) \) that are produced by selective etching of the A layer atoms (i.e., Al) from MAX phases (i.e., \( \text{V}_\text{2} \text{AlC} \)), a large group of layered ternary carbides and nitrides. \(^2\) Despite their high capacities, the MXene cathodes reported in our previous work showed severe capacity decay in over hundreds of cycles. Here, we report the results of our recent research on addressing this problem through a combination of designing new electrode architectures and modifying electrolyte composition. This approach results in achieving highly stable performance for MXene cathodes over hundreds of cycles. We demonstrate the fabrication of freestanding and binder-free hybrid electrode materials based on different 2D MXene compositions with exceptional volumetric capacities and long cycle life. We also present the results of our investigation of thermodynamics and kinetics of Al\(^3+\) intercalation into MXene cathodes through various structural characterizations (XRD, SEM, HRTEM, and XPS) and electroanalytical techniques such as Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Impedance spectroscopy (EIS). Our research results provide invaluable insights into the mechanism of multivalent-ion intercalation into MXenes. In addition, considering that family of the MXenes now include 20 different compositions, this research guides fabrication of an entire group of cathode materials for rechargeable aluminum batteries based on these 2D materials.

References:

2:15 PM ES02.11.03
Intercalation Host Using Defective FePO\(_4\)-Carbon Composite for Multivalent Rechargeable Battery Cathode
Yuki Orikasa; Kazuaki Kimi; Etsuro Iwama; Wako Naoi; Yusuke Yamaguchi; Yoshihito Yamaguchi; Koji Ohara; Patrick Rozier; Patrice Simon and Katsuhiro Naoi; Ritsumeikan University, Kusatsu, Japan; Tokyo University of Agriculture & Technology, Koganei, Japan; K & W Inc., Kunitachi, Japan; Japan Synchrotron Radiation Research Institute (JASRI, SPring-8), Sayo, Japan; Centre national de la recherche scientifique, Toulouse, France.

Multivalent ion rechargeable batteries are promising candidates as the next generation of rechargeable battery technologies. The advantages of metal anode such as magnesium or calcium are their high theoretical capacity, available stocks and the absence of dendrite formation. However, multivalent ions exhibit slow diffusion kinetics in solid electrodes and intercalation hosts that can operate at room temperature are currently limited to Chevrel structure type compounds.\(^1\)

In this study, we investigated the use of FePO\(_4\)-carbon composite prepared by ultratrefugination (UC) method as multivalent-ion host structure. For nano-hybrid capacitor electrode, the electrode materials prepared by the UC method reported so far are capable of ultrafast lithium-ion insertion and extraction reaction.\(^2\) Therefore, we used the UC method to prepare materials as host electrode for multivalent-ion intercalation. Since the irreversible magnesium ion insertion-extraction reaction in olivine type FePO\(_4\) crystal has been reported,\(^3\) in our study, non-crystalline FePO\(_4\) with carbon composite was used. FePO\(_4\)-carbon composite was prepared by UC process.\(^2\) The composite was mixed with PTFE, with a weight ratio of 9:1. The electrodes were firstly charged in 1M LiPF\(_6\) in a 3:7 volume ratio of ethylene carbonate and diethyl carbonate. Then, a three electrode cell with an Ag/Ag\(^+\)/Mg double junction reference electrode was assembled using the previously charged FePO\(_4\)-carbon composite electrode. The counter electrode was an active carbon, and the electrolyte was 0.5 M magnesium bis(trifluoromethanesulfonfonyl)imide in acetonitrile. Charge-discharge measurements were performed at 25°C. The valence state of Fe and local structure in the charged / discharged electrodes were tracked by X-ray absorption spectroscopy, which was measured in a transmission mode.

Reversible charge / discharge capacity was observed after the first discharge. At 25°C, a capacity of approximately 150 mAh per weight of active material at a rate of 1/20 C was achieved at a potential of about 2 V versus Mg\(^+/\text{Mg}\). From TEM-EDX measurements, FePO\(_4\) particles were found to be embedded in carbon and the intensity of magnesium was observed only in regions where FePO\(_4\) particles exist. X-ray absorption edge at Fe K-edge shifts downward in energy during discharge, reflecting the reduction of iron ions to maintain electrical neutrality upon magnesium-ion insertion in the discharge reaction. In the presentation, we will also report about the charge-discharge characterizations of FePO\(_4\)-carbon composite in calcium and zinc ions based electrolytes.

References:

2:30 PM ES02.11.04
Real-Time Identification and Understanding of Zinc Compounds in Rechargeable Zinc Electrodes
Brendan E. Hawkins, Damon Turney, Gautam Yadav and Sanjoy Banerjee; The City College of New York, New York, New York, United States.

Rechargeable zinc electrodes are attractive forms of energy storage for commercial applications because of their high theoretical energy capacity and their use of inherently cheap, safe, and environmentally friendly materials. The zinc rechargeable electrode in commercial batteries is historically limited in depth of discharge and cycle life, which has prevented them from being widely used on a commercial scale. This limitation is partly due to irreversible reactions occurring during discharge, which lead to passivation of the zinc electrode. Despite extensive study, the properties of these oxide species and the conditions leading to their formation are not fully understood. In this work, using in-operando optical microscopy, we have identified various zinc oxide morphologies in alkaline electrodes classified as Type I and Type II in the literature as well as other species that have not yet been identified. We will further analyze these zinc compounds using in-operando x-ray diffraction and scanning electron microscopy, and chemically identify these species and the conditions at which they form using in-operando confocal Raman spectroscopy. Identification of zinc species that detrimentally affect zinc rechargeablebility and understanding their formation will promote the design of better zinc electrodes and electrodes, leading to improved cycle life and depth of discharge in zinc batteries.

2:45 PM BREAK
Electrochemical energy storage was an important enabler of the wireless revolution and it is touted as a key component of a society that shifts away from its dependence on fossil fuels. Li-ion batteries are the primary technology when high energy devices are required. However, despite their improved functionality over older systems (e.g. lead-acid car batteries), they do not quite yet meet the emerging energy demands in transportation and grid markets. This roadblock sparked interest in the development of batteries that utilize Mg\(^{2+}\) as ionic carrier. Theoretical predictions indicate that couples exist between a Mg metal negative electrode and oxide positive electrodes that could surpass the current practical limits of current devices. Among the candidate oxides, those showing a spinel structure have been predicted as the most suitable for the reversible intercalation of ions such as Mg\(^{2+}\) or even Ca\(^{2+}\) [1], the critical reaction in the positive electrode. However, experimental validation, while incipient [2], has not been fully achieved. In this talk, we will present the most up-to-date insight into the ability of spinel oxides to diffuse and reversibly intercalate Mg\(^{2+}\). In this task, the ability to synthesize particles at small dimensions is vital, as is the characterization of chemical and physical phenomena using a combination of tools providing information at different scales. We will rely on data from X-ray diffraction, spectroscopy and scattering, electron microscopy and nuclear magnetic resonance to probe the reactions that occur when spinel oxides are used as working electrodes in cells with electrolytes containing Mg\(^{2+}\). The rationale for the choice of techniques and the key pieces they provided to complete the picture will be discussed. Our ultimate aim in the talk will be to establish relationships between crystal-chemistry, charge carrier and outcomes of the electrochemical reaction.


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**Thursday Afternoon, April 25, 2019**

**PCC North, Room 126 C**

**3:15 PM ES02.12.01**

**Measuring and Defining Electrochemical Reactions of Transition Metal Oxides in Mg Electrolytes**

Jordi Cabana; University of Illinois at Chicago, Chicago, Illinois, United States.

Electrochemical energy storage was an important enabler of the wireless revolution and it is touted as a key component of a society that shifts away from its dependence on fossil fuels. Li-ion batteries are the primary technology when high energy devices are required. However, despite their improved functionality over older systems (e.g. lead-acid car batteries), they do not quite yet meet the emerging energy demands in transportation and grid markets. This roadblock sparked interest in the development of batteries that utilize Mg\(^{2+}\) as ionic carrier. Theoretical predictions indicate that couples exist between a Mg metal negative electrode and oxide positive electrodes that could surpass the current practical limits of current devices. Among the candidate oxides, those showing a spinel structure have been predicted as the most suitable for the reversible intercalation of ions such as Mg\(^{2+}\) or even Ca\(^{2+}\) [1], the critical reaction in the positive electrode. However, experimental validation, while incipient [2], has not been fully achieved. In this talk, we will present the most up-to-date insight into the ability of spinel oxides to diffuse and reversibly intercalate Mg\(^{2+}\). In this task, the ability to synthesize particles at small dimensions is vital, as is the characterization of chemical and physical phenomena using a combination of tools providing information at different scales. We will rely on data from X-ray diffraction, spectroscopy and scattering, electron microscopy and nuclear magnetic resonance to probe the reactions that occur when spinel oxides are used as working electrodes in cells with electrolytes containing Mg\(^{2+}\). The rationale for the choice of techniques and the key pieces they provided to complete the picture will be discussed. Our ultimate aim in the talk will be to establish relationships between crystal-chemistry, charge carrier and outcomes of the electrochemical reaction.

**SYMPOSIUM ES03**

**TUTORIAL:** Advanced Characterizations for Energy Materials  
April 22 - April 22, 2019

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* Invited Paper

**TUTORIAL**  
Advanced Soft X-Ray Spectroscopy and Cryo-TEM in Studies of Batteries and Electro catalysts  
Monday Afternoon, April 22, 2019  
PCC North, 100 Level, Room 126 B

This tutorial focuses on the fundamentals and applications of several advanced characterization techniques to understand the atomic and electronic structures of energy materials, especially batteries and electrocatalysts. The tutorial will include detailed explanations of recent advances and developments in soft X-ray spectroscopy, including soft X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and high-efficiency mapping of resonant inelastic X-ray scattering (mRIXS) with in-situ operando capabilities. The second part of the tutorial will focus on cryogenic electron microscopy and spectroscopy of energy materials with emphasis on reactive materials and liquid-solid interfaces. Fundamental and practical aspects of cryo-focused ion beam milling (cryo-FIB), cryo-scanning transmission electron microscopy (cryo-STEM), electron energy loss spectroscopy (EELS) and spectroscopic mapping will be discussed. Two invited speakers, Wanli Yang from Lawrence Berkeley National Laboratory and Lena F. Kourkoutis from Cornell University, will highlight examples of these techniques used in their energy materials research in addition to providing details on principles. The tutorial will therefore cover both fundamentals and frontier research, and emphasize the strategies to use proper tools for the studies of electrochemical energy systems under extreme conditions.

1:30 PM  
**Advanced Soft X-Ray Spectroscopy of Energy Storage Materials**  
Wanli Yang; Lawrence Berkeley National Laboratory

This course is intended for chemists, physicists, materials scientists, and engineers with an interest in applying advanced soft X-ray techniques to study a broad variety of electrochemical materials. The highlight will be on the recent developments of high-efficiency mapping of resonant inelastic X-ray scattering (mRIXS) for studying energy materials, but conventional X-ray emission spectroscopy (XES) and five different channels of soft X-ray absorption spectroscopy (sXAS) will be explained in details. The attendee will develop a basic understanding of these modern soft X-ray spectroscopic techniques, the proper data interpretations, and their pros and cons, with plenty of examples on energy storage material studies.

3:00 PM BREAK

3:30 PM  
**Cryogenic Electron Microscopy for Electrochemical Systems**  
Lena F. Kourkoutis; Cornell University

This lecture will cover the principles of cryogenic electron microscopy and spectroscopy of energy materials with emphasis on reactive materials and liquid-solid interfaces. Fundamental and practical aspects of cryo-focused ion beam (cryo-FIB), cryo-scanning transmission electron microscopy (cryo-STEM) and electron energy loss spectroscopy (EELS) will be discussed including signal interpretation, artifacts and limits of each technique. Examples of structural and chemical mapping of processes at solid-liquid interfaces in lithium-metal batteries will be provided and will demonstrate the potential of cryogenic electron microscopy for probing nanoscale processes at intact solid-liquid interfaces in functional devices for energy applications.

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**SYMPOSIUM ES03**

Electrochemical Energy Materials Under Extreme Conditions  
April 23 - April 25, 2019

Symposium Organizers  
Hye Ryung Byon, Korea Advanced Institute of Science and Technology  
Zhenxing Feng, Oregon State University  
Cynthia Lundgren, U.S. Army Research Laboratory  
Hua Zhou, Argonne National Laboratory

Symposium Support  
Army Research Office

* Invited Paper

**SESSION ES03.01:** Catalytic and Energy Conversion Processes Under Various Environments  
Session Chairs: Ren Yang and Hua Zhou  
Tuesday Morning, April 23, 2019  
PCC North, 100 Level, Room 126 B

10:30 AM *ES03.01.01*  
**Highly Stable Carbon-Based Catalysts for Bifunctional Oxygen Reduction and Evolution for Reversible Alkaline Fuel Cells**  
Gang Wu; State University of New York at Buffalo, Buffalo, New York, United States.
The intrinsic instability of carbon largely limits its use for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) as a bifunctional catalyst in reversible fuel cells or water electrolyzers. Herein, we discovered that Mn doping has a promotional role in stabilizing nanocarbon catalysts for the ORR/OER in alkaline media. Stable nanocarbon composites are derived from an inexpensive carbon/nitrogen precursor (i.e., dicyandiamide) and quaternary FeCoNiMn alloy via a template-free carbonization process. In addition to FeCoNiMn metal alloys/oxides, the carbon composites comprise substantial carbon tube forests growing on a thick and dense graphite substrate. The dense carbon substrate at high degree of graphitization results from Mn doping, while active nitrogen-doped carbon tubules stem from FeCoNi. Catalyst structures and performance are greatly dependent on the doping content of Mn. Various accelerated stress tests (AST) and life tests verify the encouraging ORR/OER stability of the nanocarbon composite catalyst with optimal Mn doping. Extensive characterization before and after ASTs elucidates the mechanism of stability enhancement resulting from Mn doping, which is attributed to (i) hybrid carbon nanostructures with enhanced resistance to oxidation and (ii) the in situ formation of the β-MnO2 and FeCoNi-based oxides capable of preventing carbon corrosion and promoting activity. Note that the improvement in stability due to Mn doping is accompanied by a slight activity loss due to a decrease in surface area. This work provides a strategy to stabilize carbon catalysts by appropriately integrating transition metals and engineering carbon structures. 

11:00 AM *ES03.01.02
Interfacial Bonding Layer for High Mechanical and Chemical Robustness of Polymer Electrolyte Fuel Cells for Vehicle Applications Hoe-Tak Kim1, 2, 3, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of); 4Advanced Battery Center, KAIST Institute for the NANOCentury, Daejeon, Korea (the Republic of).

Polymer electrolyte fuel cells (PEMFCs) have been considered a promising mobile energy conversion system to replace internal combustion engines due to high energy conversion efficiency, moderate operating temperature, short fuel charging time, and zero emission. Accordingly, PEMFC is one of the promising candidates for vehicle electrification as exemplified by fuel cell electric vehicle. Even though PEMFC technology has arrived at a commercialization stage, the durability of fuel cell stack needs to be further improved to guarantee reliable operations under harsh conditions. Various degradation modes critical to the durability have been identified, the hydroxyl radical formed by crossover H2 or O2 in the presence of Pt catalyst deteriorates membranes and-ionomers in the catalyst layers; the stress generated during dynamic change in hydration level of the cell leads to a mechanical defect at the membrane/catalyst layer interface or membrane. These chemical and mechanical degradation issues, which eventually result in a cell failure, still remain unsolved. During the past few years, we have addressed the durability problems of PEMFC by engineering the membrane/catalyst layer interface. We witnessed that the interfacial durability between membrane and catalyst layer can be improved by introducing an interfacial bonding layer such as Lego-block structured and ball-socket joint structured interfaces, enhancing the humidity cycling stability. Recently, we find new possibilities that interface material and structure design can also improve the mechanical and chemical durability of membranes. In this talk, we will present our results on how the fuel cell durability under harsh conditions can be improved by advanced interfacial engineering.

11:30 AM ES03.01.03
3D Graphene-Coated Ni Foam Heterostructures as Bipolar Plates of a Polymer Electrolyte Membrane Fuel Cell Yeoseon Sim1, Jinsung Kwak1, Se-Young Kim1, Yongsu Jo1, Seunghyun Kim1, Sung Yoush Kim1, Ji Hyun Kim2, Chi-Seung Lee1, Jangho Jo2 and Soon-Yong Kwon1, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2Hyundai Motor Group, Yongin, Korea (the Republic of).

The polymer electrolyte membrane fuel cell (PEMFC), which is an energy technology for directly transforming chemical energy into electrical energy by oxidizing hydrogen at the anode and reducing oxygen at the cathode, is a promising way to resolve the energy crisis and environmental pollution. However, realizing their implementation as a practical and highly efficient energy conversion system remains a big challenge because the chemical instability of metal bipolar plates in the harsh acidic (pH ~3-5) and humid operating environment inside PEMFCs leads to decreased performance and durability. To improve the chemical durability of metal plates, various protective layers such as TiC, CrC, and TiN/CrN have been applied to their surfaces.1,2 Even though the corrosion resistance of metal bipolar plates coated with protective layers has been enhanced, their contact resistances remain above the target value for PEMFCs (PEMFC targets for 2020 set by the US Department of Energy (DOE): interfacial contact resistance < ~10 mΩ cm2 and corrosion current density < ~1 µA cm2).1 Besides, another obstacle to commercial utilization of metal bipolar plates is the difficulties in precise machining and designing of flow channels used as a distributor of reactant gases on the metal plate. In this work, we present a novel method for coating highly crystalline multilayer graphene (Gr) as a superficial protective layer (thickness of ~12 nm) onto a 6 × 6 cm2 Ni foam in short growth times (t ≤5 min) via the facile and rapid thermal annealing (RTA) of poly(methylmethacrylate) as a solid-state C source. The synthesized graphene layers have a low defect density and completely cover the three-dimensional (3D)-structured surface of the Ni foam, dramatically improving its corrosion resistance, interfacial contact resistance (ICR), and hydrophobicity. After stability tests in the operating environment of a PEMFC, the optimized Gr-coated Ni foam preserved its exceptionally low corrosion current density of 2.5 µA cm2 with an ICR of 9.3 mΩ cm2 at 10.1 kgf cm2. A H2-air PEMFC fabricated using the Gr-coated Ni foam as bipolar plates showed an exceptionally enhanced maximum power density of ~967 mW cm2, which is the best among those of the reported metal foam bipolar plates. Moreover, all the characteristic values meet the 2020 DOE technical target values for transportation applications of PEMFCs. This study demonstrates that the 3D Gr-coated Ni foam prepared using our proposed new coating method exhibits superior characteristics as an inhibitor for the highly efficient performance of a PEMFC with durability. Our facile coating approach can pave the way to further enhance energy conversion systems through interface engineering.

Reference
100 °C, depending on the thermal management provided in the spacecraft. On the other hand, atmospheric missions and surface missions on inner planets, e.g., Venus, require power technologies that can survive high temperatures up to 465 °C. Another unique requirement for the power sources in NASA missions, especially missions to Jupiter and its moons, is tolerance to high intensity radiation environment of ~10 Mrad. Further, for the missions to Ocean Worlds that are more likely to have extant life, e.g., Europa, Titan and Enceladus, the power sources need to be biologically sterile, which is currently accomplished only by irradiation to about 10 Mrad.

In support of these various missions, we developed, and are still developing in some cases, different primary and rechargeable battery technologies for extreme environments. The primary battery technologies have been developed include lithium-thionyl chloride cells for operations at -80°C, similar lithium oxyhalide chemistries for lower operating temperatures of -100 °C, and lithium-carbon fluoride batteries with high specific energy of >700 Wh/kg and good radiation tolerance. The rechargeable battery technologies that have been advanced include low temperature lithium-ion chemistries operating at low temperatures of -40 to -70 °C and high specific energy candidates offering high specific energy of 220 Wh/kg or higher combined with tolerance to ~20 Mrad of radiation. Finally, we have also focused, to less extent, on high temperature sodium rechargeable molten salt batteries with metal chloride cathode operational at 20-350 °C and lithium molten salt primary batteries that can survive and operate at 465 °C. In this paper, we will briefly describe these technological advances on energy storage technologies for extreme environments in conjunction with the mission descriptions.

2:00 PM ES03.02.02
Novel Molecular Designing of High-Performance Bio-Based Polybenzimidazoles to Prepare Single-Ion Conducting Solid Polymer Electrolyte
Aniruddha Nag, Md Asif Ali, Raman Vedaranjan, Noryoshi Matsumi and Tatsuaki Kaneko; Japan Advanced Institute of Science and Technology, Nomi, Japan.

Conventional bio-based plastics are usually low performance plastics in terms of thermo-mechanical properties. Here we have successfully synthesized bio-based polybenzimidazoles consist of high thermo-mechanical properties comparable with engineering plastics, owing to strong π-stacking interaction among aromatics and imidazole rings and H-bonding between N-H and N of imidazole ring. Imidazole proton can be easily modified by various substituents. Here we report N-boronation of the PBI via lithiation to be ionically conductive (scheme 1). The PBI was modified by triethylborane substitution to imidazole proton to create boronated PBI (B-PBI) with Li counter ion. Ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIMTFSI) was added to the B-PBI as a plasticizing agent with different concentration to prepare composite solid polymer electrolytes (SPEs). Impedance analysis of various composition SPEs show ionic conductivity with 1.4x10^-2 S/cm at maximum whereas Li-ion transference number was obtained (t_li^+) = 0.623 at maximum. Ionic conductivity, Li-ion transference number, and carrier ion number increased with increasing amount of BMIMTFSI, to show maxima at a certain concentration. Further, charge-discharge measurement was performed by fabricating anode half-cell composed of the highest li-ion conducting composite SPE as electrolyte, Si-electrode as anode, and Li-metal as cathode. The resulting value showed a good reversible capacity at discharge rates ranging 0.1 – 2.0 C and stable solid electrolyte interface formation takes place.

2:15 PM ES03.02.03
Proton Transport in Solid Electrolytes Under High Pressure
Artur Braun1 and Qianli Chen1,2,3; 1Empa, Dubendorf, Switzerland; 2State Key Laboratory of Metal Matrix Composites, University of Michigan-Shanghai Jiao Tong University Joint Institute, Shanghai, China; 3Physics, ETH Zürich, Zürich, Switzerland.

Protons are the relevant electric charge carriers in the sustainable hydrogen economy [1]. Because of humidity (H2O) in ambient environment and the crystalline imperfections (defects) in materials, water molecules like to enter some materials and settle as hydrates or hydrides structures. Oxygen and protons become part of the structure. Upon thermal excitation, hydroxyl bonds may become hydrogen bonds which eventually “melt”. The protons may then liberate and become electric charge carriers, which lend them a particular function in solid electrolytes as proton conductors. We have in the last couple of years observed and investigated the biography and lifestyle of such protons from localization to de-localization. The proton is an elusive player and not always easy to make out. With a combination of neutron and synchrotron based scattering and spectroscopy methods, along with electroanalytical techniques, we have increased our understanding of the proton dynamics and its structural origin, which is important for super-protonic conductivity. We have investigated the oxygen vacancy filling of engineered oxygen deficient proton conductors by water molecules with impedance spectroscopy and ambient pressure XPS [2], which enabled us to sketch a detailed picture of the correlation of molecular and electronic structure changes, with concomitant onset of proton conductivity at higher temperatures. We thus could design experiments, where the proton-phonon coupling was quantitatively investigated with high pressure and high temperature impedance spectroscopy combined with quasi-elastic neutron scattering [3,4]. Supported by pressure dependent XRD and Raman scattering [5,6] we correlated the proton jumping parameters with the temperature and found that the proton jump times follow a polaron relation [Braun 2017] [7,8,9].

Related Publications:

3:00 PM ES03.02.04
Lithium-Sulfur Batteries—The Next Frontier in Energy Storage
Nikhil Koratkar; Rensselaer Polytechnic Institute, Troy, New York, United States.

Lithium-sulfur (Li-S) batteries offer a theoretical energy density of ~2600 Wh/kg (compared to ~387 Wh/kg for Li-ion technology) and therefore offer great potential as a next generation energy storage device. However there are two major barriers to realization of high performance Li-S batteries: (1) poor cycle stability caused by dissolution of intermediate lithium polysulfides from the S cathode into the electrolyte and (2) nucleation and growth of dendritic structures on the Li metal anode, which can electrically short the battery. In this talk, I will discuss some possible solutions to these problems. Specifically, I will show that two-dimensional (2D) sheets of black phosphorous (i.e. phosphorene) are highly effective as a lithium polysulfide trapping agent. I will further show that the Li dendrite problem can be addressed by using self (Joule) heating to accelerate surface diffusion processes to heal (smoothen) the dendrites in situ. Such advances show potential in enabling the successfully deployment of Li-S batteries with breakthrough improvements in performance as compared to the incumbent Li-ion technology.

Related Publications:

3:30 PM ES03.02.05
Rational Design and Synthesis of Nanostructured Hybrid Cathode Materials for Lithium-Sulfur Batteries
Yanglong Hou, Muhammad Asif and Zeehan Ali; Peking University, Beijing, China.

Lithium-sulfur batteries (LSBs), have been considered as promising power source for future electric vehicles (EVs) due to their high energy and power densities. Thus, many efforts have been made on new electrode materials that can bring the realization of these devices. Despite offering many fascinating advantages over conventional lithium-ion batteries (LIBs), such as low cost of sulfur, the safer operating voltage and in particular non-toxic nature, LSBs are facing numerous challenges, which are currently hindering LSBs from being a serious competitor to LIBs on commercial scale. Among the mainstream challenges, the polysulfide shuttle effect, insulating nature of sulfur, volume expansion, and self-discharge are very crucial factors which need to be resolved urgently to improve the electrochemical performance of LSBs. Moreover, structural disintegration,
limited access to redox sites and loss of electrical contact have long been identified as common reasons for capacity loss and poor cyclic life of these materials. Thus, rational design can inhibit the side reaction by surface protection, make all redox sites accessible by increasing the intrinsic conductivity of the active materials, maintain a continues cycle life of the battery and the charging algorithm will be adjusted accordingly, therefore making the charging algorithm adaptive. This type of charging should help reduce charging time for commercial lithium-ion batteries and also help improve the cycling life of the battery.

4:45 PM ES03.02.09
Microstructural Complexations in Extreme Fast Charging of Li-Ion Batteries Antarsho Mishry and Partha P. Mukherjee; Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States.

Widespread acceptance for electric vehicles is deterred by (i) range anxiety and (ii) recharging time. To be competitive with conventional fuels, battery recharging time must be less than 10 min, which amounts to a very high charging rate (~6C). At such high rates (i.e., extreme fast charge, XFC), a host of anode centric issues arise, namely suboptimal charging capacity, self-heating, and irreversible plating losses. Fundamentally these observations are a result of sluggish kinetic and transport modes at the pore scale. Here in we analyze such complex physicochemical interactions for different commercial graphite electrodes (microstructures are obtained through tomography). Even though the porosity of these structures is spatially quite uniform, the pore and solid networks exhibit considerable variations, both within the sample and across electrodes. Based on these examinations, we outline the guidelines for improving the XFC response via appropriate scaling of structural features.

SESSION ES03.03: Understanding Fundamental Processes and Interactions at Electrode and Electrolyte Interfaces
Session Chairs: Erik Brandon and Chengjun Sun
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 126 B
The Role of Interlayer Structural Water During Ion Intercalation in Crystalline Transition Metal Oxides

Brownmillerite (BM)-structured SrCoO\(_2\) oligomers backbone at the silicon surface is a key factor. Through these studies, we find that the formation of a robust nanostructure SEI made of a Li-ion conductive solid conductor oxide solid fuel cells (H-SOFC) by using Synchrotron Infrared Nanospectroscopy (SINS) and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the Advanced Light Source.

To unravel the mechanism behind an effective Solid electrolyte interphases (SEI) layer on Si anode, we used the unparalleled spatial resolution and surface sensitivity of the near-field IR probe (ca. 20 nm) and chemical selectivity of SINS. We leverage the influence of LiBOB additive to shed lights on SEI’s crucial components and structure at a nanoscale level, which corresponds to the size of the SEI building blocks. Through these studies, we find that the formation of a robust nanostructure SEI made of a Li-ion conductive oligomers backbone at the silicon surface is a key factor.

We also examined proton and oxygen transport at the interface between a standard H-SOFC perovskite electrolyte (BaCe\(_{0.8}\)Zr\(_{0.2}\)O\(_{3-\delta}\)) and the fuel by using Synchrotron Infrared Nanospectroscopy (SINS) and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS).

In Situ Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the Advanced Light Source.

Performance of electrochemical systems is governed by ion transport through solid/liquid or solid/gas interfaces. Major breakthroughs are then intrinsically linked to a detailed understanding of how molecules, atoms, and electrons behave at these interfaces during operation. Recent progress in the development of ex situ and in situ characterization surface techniques using synchrotron radiation sources has enabled major scientific advancements toward this understanding. In this work, we studied interfacial processes in energy materials such as Li-ion systems or protonconductor oxide solid fuel cells (H-SOFC) by using Synchrotron Infrared Nanospectroscopy (SINS) and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at the Advanced Light Source.

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It is increasingly recognized that extremely fast charging and discharging, along with long cyclability, will require energy storage materials that are able to respond with minimal mechanical deformation while at the same time storing significant amounts of energy. Our research shows that interlayer structural water in crystalline transition metal oxides appears to play an important role in mitigating the mechanical deformation during electrochemical ion intercalation in a class of model transition metal oxides, layered tungsten oxide hydrates. We investigated the electro-chemo-mechanics of proton intercalation into crystalline WO\(_3\) and crystalline, layered WO\(_3\)\(\bullet\)2H\(_2\)O using operando atomic force microscopy (AFM) dilatometry. The nanoscale deflections of the AFM tip were measured for both WO\(_3\) and WO\(_3\)\(\bullet\)2H\(_2\)O as a function of potential and cyclic voltammogram sweep rate for charge/discharge times on the order of minutes and seconds, pressing the extremes of fast charging and discharging of electrochemical energy storage materials.

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Interfacial reaction of LCO in the aqueous electrolyte solution is still superficial however.

Here we present degradation phenomena of LCO electrode in aqueous medium using various X-ray measurement techniques, and suggest the solution to avoid such an irreversible electrochemical reaction. The aqueous solution was prepared with 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and pH was controlled to ~6.8 and 10. In both cases, there was no evidence for the formation of cathode-electrolyte interphase (CEI) on LCO in contrast to the one with non-aqueous electrolyte solution. The direct contact of aqueous electrolyte solution to LCO surface results in the short-range disorder of LCO structure such as the distortion of octahedral CoO₆.

Since the risk of catch fire using nonelectrolyte aqueous solution, aqueous solution-based rechargeable lithium batteries (ARLB) have been highlighted. However, the conventional positive electrodes of lithium transition-metal oxide such as LiCoO₂ (LCO) and LiNi₀.₅Mn₀.₅O₂ (NMC) have suffered from poor cyclability in aqueous medium. Representatively, the layered two-dimensional structure of LCO shows notably poor stability, possibly due to the surface degradation from water and proton. The understanding of interfacial reaction of LCO in the aqueous electrolyte solution is still superficial however.

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batteries, achieving 80% state of charge in ten minutes. Next, we rationalize their high performance via cell-level simulations and electrode-level physical characterization. Our results reveal that loss of active material from the graphitic negative electrode is a significant source of degradation, preceding more conventional fast charging degradation modes such as lithium plating. We also identify a critical charge rate beyond which the loss of active material, and thus the overall cell degradation, accelerates. Finally, we study the rate of SEI growth during fast charging via electrochemical methods, identifying a strong dependence on the applied C rate. This work provides novel insight into optimizing and characterizing extreme battery fast charging for time-sensitive applications and suggests avenues to improve both charging times and lifetimes during aggressive battery operation.

11:45 AM ES03.03.10
High-Performance Electromechanical Device via Controlling Charge Injection Pham S. Nguyen1, Young-hun Seo1, Hong Chul Lim2, Haeun Lee1, Truong Khac Phu Cuong1, Ji-young Lee1 and Ik-Soo Shin1; 1Soongsil University, Seoul, Korea (the Republic of).

Here, we report in-depth study on basic principles of electrochemical devices (ECD) such as their structural design as well as operational method. Electrochemically deposited prussian blue (PB) and tungsten trioxide (WO3) thin films were employed as a working and counter electrode, respectively, and sandwich-type ECDs were fabricated using aqueous electrolyte. Electrochemical devices relying on interfacial charge-transfer and ion transport, normally suffer from a decline of its operational performance which is caused by irreversible redox reaction, ion accumulation or overvoltage at the solution/electrode interface, and it severely curtails the operational lifetime of the devices. After careful investigation of the redox properties of PB and WO3 films and their complementary ECDs, we found that by balancing the charge during on/off switching (regarding bleaching and coloration), the ECD could exhibit improved long-term stability with broad optical modulation and decent coloration efficiency (G.T < 1.7% over 2000 cycles) under mild operational voltage. We expect that the results provide a general overview of the operational conditions and structural design in ECD researches.

SESSION ES03.04: Promoting Advanced Battery Electrodes for Auto Mobility and Stationary Storage
Session Chairs: Yingge Du and Tim Fister
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 126 B

1:30 PM *ES03.04.01
Ion Transport and Electrochemistry in Battery Electrolytes Over Wide Range of Salt Concentrations Ole Borodin, Jenel Vatamanu, Travis Pollard and Kenneth W. Leither; U.S. Army Research Laboratory, Adelphi, Maryland, United States.

This presentation will focus on the molecular scale understanding of key factors influencing ion transport, electrochemical stability and decomposition in a wide range of aqueous and non-aqueous electrolytes as a function of salt concentration. No one simulation technique is capable of efficiently capturing all transport and electrochemical properties at interfaces. Therefore, we will utilize a combination of a) density functional theory (DFT) studies of the solvent reactions on cathode surfaces and at the solid electrolyte interphase (SEI) covering lithium metal; b) representative quantum chemistry (QC) calculations performed on the representative small model electrolyte clusters to estimate oxidation and reduction; c) molecular dynamics (MD) using APPLE&P polarizable force field to examine bulk and interfacial properties of electrolytes and electrochemical interfaces. Combined together, information from these modeling studies expands on the previous work and suggests numerous strategies for stabilizing the electrolyte – electrode interfaces for a number of aggressive high energy density cathodes combined coupled with graphite and metal anodes.

References

2:00 PM ES03.04.02
High Temperature vs High State-of-Charge—Optimizing the Triad of Energy Density, Cycling Rate and Lifetime Clement Bonniel1,2 and Daniel Steingart1,2,3; 1Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; 2Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

Enabling fast-charging capabilities in lithium-ion batteries (LIBs) is critical to the continued development of modern applications such as electric vehicles (EVs), unmanned robots, and grid-leveling applications. However, the current state-of-the-art in commercially available LIBs renders fast charging difficult, especially if energy density, and a long battery lifetime are also desired. While many researchers are currently looking for novel materials to alleviate this issue, this research takes a different approach: can we use currently available materials as an attractive alternative RFB technology because redox active organic molecule materials are synthetically tunable, sustainable, and potentially low cost. The presentation will highlight our research efforts in developing viologen anolyte materials for both anion and cation exchange AORFBs with a variety of catholyte materials including ferrocene, TEMPO, ferrocyanide, and halides. The viologen AORFBs demonstrated outstanding battery performance including a power density up to 120 mW/cm², energy efficiency up to 72% at 60 mAh/cm², and capacity retention up to 99.999% per cycle up to 1000 cycles, representing the state of the art organic RFBs. Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow batteries for large scale and dispatchable

1:25 PM ES03.04.03
Graphite Lithiation Under Fast Charging Conditions—Atomistic Modeling Insights Juan C. Garcia, Hakim Iddir and Dennis Dees; Argonne National Laboratory, Lemont, Illinois, United States.

The general public reception of electric vehicles (EV) depends, among other factors, on meeting their expectations of similar comfort compared to conventional vehicles. Replicate the convenience of filling a tank of fuel in minutes is a very challenging task when one has to recharge a Li-ion battery. The primary goal of a fast charging protocol must be avoiding Li plating in the anode and maintaining temperature under control. Hence, a deeper understanding of the thermodynamics and kinetics of the anode charging process is crucial to improve the models and subsequently the design of battery cells. In the present work, an atomistic level analysis of Li intercalation and diffusion in graphite have been performed under fast charging conditions. In this presentation, we will show and discuss the effect of fast charging conditions on the intercalation and diffusion mechanism of Li in graphite.

The authors gratefully acknowledge support from the U. S. Department of Energy (DOE), Vehicle Technologies Office. Computer time allocations at the Argonne's Laboratory Computing Resource Center is gratefully acknowledged. Argonne National Laboratory is operated for DOE Office of Science by UChicago Argonne, LLC, under contract number DE-AC02-06CH11357.

2:30 PM BREAK

3:30 PM *ES03.04.04
Aqueous Organic Redox Flow Batteries for Large-Scale and Dispatchable Energy Storage Bo Hu, Jian Luo, Camden Debruler, Maowei Hu, Wenda Wu and Tianbiao Liu; Utah State University, Logan, Utah, United States.

Redox flow batteries have several outstanding technological advantages over traditional static batteries (e.g. Li ion and Lead acids) for large scale energy storage including decoupled energy and power, safe energy storage, high current and powerful performance, and scalability. Recently, Aqueous organic redox flow batteries (AORFBs) have emerged as an attractive alternative RFB technology because redox active organic molecule materials are synthetically tunable, sustainable, and potentially low cost. The presentation will highlight our research efforts in developing viologen anolyte materials for both anion and cation exchange AORFBs with a variety of catholyte materials including ferrocene, TEMPO, ferrocyanide, and halides. The viologen AORFBs demonstrated outstanding battery performance including a power density up to 120 mW/cm², energy efficiency up to 72% at 60 mAh/cm², and capacity retention up to 99.999% per cycle up to 1000 cycles, representing the state of the art organic RFBs. Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow batteries for large scale and dispatchable
We report the synthesis of MnVO$_3$ power density, high energy density, and improved charge/discharge rates. Significantly improve the supercapacitor’s performance is the nano-structuring of the electrode material, which considerably increases their surface area. Different morphologies of electrode materials include mesoporous carbon, metal-organic frameworks, and transition metal oxides (TMOs) with a perovskite structure. TMOs store charges electrochemically. Although TMOs are considered the ideal electrode materials for supercapacitors, their fast charge/discharge rates make them the perfect storing devices. However, supercapacitors still face obstacles such as low energy density, performance degradation, and high cost. The active materials of the supercapacitors’ electrodes determine the supercapacitor’s energy storage capacity and electrochemical performance. Accordingly, new materials are being researched every day for the purpose of enhancing the supercapacitor’s performance. Of the most extensively studied materials today are graphene, carbon nanotubes, and transition metal oxide nanofibers (TM OnF) with embedded metal oxide nanoparticles.

Design of Supercapacitors for Wide Temperature Operation

The world’s transition to sustainable energy has been largely accelerated from the transportation field. Thanks to the increasingly wide deployment of charging stations and government incentives, electric vehicles are seeing a fast growth in recent years. Most of them are completely or partially powered by Li-ion batteries, which store and distribute the energy whenever is the need for the operation of the vehicle. The battery pack consists of tens, hundreds, or thousands of individual cells, depending on the size (kWh) of the pack and cell as well as the form factor of the cell. As an EV start up, SF Motors is trying to produce the intelligent EV for everyone. One prominent feature of EV is their fast acceleration. A high power is delivered during fast acceleration, which requires the cell to be discharged at extreme high rates. Simultaneously, extensive heat is generated during fast acceleration, causing cells temperature increase and deteriorating electrochemical performance. For the same reason, the kinetics of the charging/discharging process are more favorable. Typical commercial devices are rated for operation between -40°C and +65°C, with temperature limits set by the nature of the electrolyte solvent. This talk will provide an update on efforts to expand beyond these temperature limits in symmetric devices through selection of suitable electrode/electrolyte materials. In addition, the potential for wider temperature operation in asymmetric cells featuring an intercalation electrode will be discussed.

Free-Standing Graphene Films Prepared via Foam Film Method for Impressive Performance Flexible Supercapacitors

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SESSION ES03.05: Poster Session
Session Chairs: Zhenxing Feng and Hua Zhou
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES03.05.01
MnVO$_3$/MnO@C Perovskite-like Binder-Free Electrospun Nanofibers as Excellent Electrodes for Supercapacitor Devices
Menna S. Said and Nageh K. Allam; The American University in Cairo, Cairo, Egypt.

Over the past decade, climate change resulted in clean energy being a primary focus in the scientific and industrial communities. With the depleting and polluting effects of fossil fuels rose the need for energy generation and storing technologies for renewable energy sources. The current commercial energy storing devices still face performance limitations, have high maintenance cost, and are not environment friendly. Electrochemical supercapacitors hold the potential of being the next generation of efficient and clean energy storing devices. Their fast charge/discharge rates make them the perfect storing devices. However, supercapacitors still face obstacles such as low energy density, performance degradation, and high cost. The active materials of the supercapacitors’ electrodes determine the supercapacitor’s energy storage capacity and electrochemical performance. Accordingly, new materials are being researched every day for the purpose of enhancing the supercapacitor’s performance. Of the most extensively studied materials today are transition metal oxides (TMOs) with a perovskite structure. TMOs store charges electrochemically. Although TMOs are considered the ideal electrode materials for supercapacitors, as they can provide both high specific capacitance and high energy density, they suffer from low conductivity and in result compromise the electrodes’ power density. Carbon based materials, on the other hand, are characterized by excellent electrical properties and high energy density. Thus, my research focuses on the synthesis of hybrid perovskite-based supercapacitors. Hybrid supercapacitors are those that combine electric double layer capacitor and pseudo-capacitor materials. The outcome should be sustainable, clean supercapacitor electrodes of high power density, high energy density, and improved charge/discharge rates.

We report the synthesis of MnVO$_3$/MnO@C perovskite-like nanofibers with embedded MnO nanoparticles of average diameter size of 400 nm. The electrospun MnVO$_3$/MnO@C electrodes achieve high specific capacitance of 1000 F/g at 5 A/g. A symmetric supercapacitor composed of MnVO$_3$/MnO@C shows an ultrahigh energy density of 23.8 Wh/kg at 5 A/g with a power density of 2500 W/kg. The device shows a superior volumetric energy density, cycle life, and capacity retention.

ES03.05.02
Free-Standing Graphene Films Prepared via Foam Film Method for Impressive Performance Flexible Supercapacitors
Zhu Yuecan and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, ChengDu, China.

Supercapacitor is regarded as the ideal power source in wearable electronic device, the electrode materials of which are always research focus due to it is a key component in the supercapacitor. Among numerous electrode materials, graphene has attracted significant attention for its outstanding electrochemical performance and mechanical properties, which endows graphene films with great potential of applications in future flexible electronics. Therefore, effective preparing methods of graphene films were researched and reported extensively in recent years. Herein, we fabricate a novel graphene oxide (GO) film with excellent mechanical properties via foam film method. Its thickness can be simply regulated by changing the concentration of the surfactant. After chemical reduction, the reduced GO (rGO) films exhibit impressive electrical conductivity of ~172 S cm$^{-1}$. The
supercapacitors based on the fabricated rGO films exhibit satisfied capacitive performance of ~56 mF cm⁻² at 0.2 mA cm⁻² with 6 M KOH solution. Furthermore, the flexible all-solid-state supercapacitors (FSSCs) based on the GO films also show great volumetric capacitance of ~2810 mF cm⁻³ at 12 mA cm⁻³ (~1607 mF cm⁻³ at 613 mA cm⁻³) with polyvinyl alcohol-KOH gel electrolyte, which indicates great rate performance of solid-state devices. Besides, the supercapacitor also show great cycling stability and flexibility: after 10000 cycles and continuously bent to 180° for 300 times, the volumetric capacitance of the FSSC remains at 81.4% and 90.4% of its initial capacitance value, respectively. All the results demonstrate the free-standing rGO films prepared via foam film method in this study could be considered as promising electrode materials for high performance flexible supercapacitors.

**ES03.05.03 Dynamic Processes in Si and Si/C Anodes in Lithium-Ion Batteries During Cycling**
Zheng-Guang Hu, Zhong Lin, Jun Chen, Ruiting Zheng and Guoan Cheng; Beijing Normal University, Beijing, China.

Si is one of the most attractive anode materials because of its extremely high theoretical capacity. In this study, we found that the (111) plane of crystalline Si in the anode is still present after 100 cycles and inferred that it is the intercalation site of Li⁺ ions. We believe that Li⁺ ions are inserted into the tetrahedral sites of crystalline Si, and the (111) plane of Si collapses and decomposes into piled crystallite lamellae; meanwhile, expansion parallel to (220) plane occurs. After full lithiation, the crystalline Si is converted to amorphous silicon. In a Si/ composite anode, although the addition of amorphous carbon improved the cycling performance of the Si anode, the activation process was prolonged as the amount of amorphous carbon increased. We determined that amorphous carbon may reduce the diffusion of Li⁺ ions, which increases the overpotential and results in the lower formation of the saturated Li/Si alloy.

**SESSION ES03.06: Flexible, Stretchable and Adaptive Energy Storage Devices for Versatile Applications**
Session Chairs: Hye Ryung Byon and Yuan Yang
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 126 B

8:00 AM **ES03.06.01 Flexible Nanocellulose Based Energy Storage Devices**
Zhaohui Wang, Petter Tammela, Ruijun Pan, Maria Stromme and Leif Nyholm; Uppsala University, Uppsala, Sweden.

The strong need for the development of inexpensive, flexible, lightweight and environmentally friendly energy storage devices has resulted in large interest in new cellulose-based electrode materials that can be used in batteries and supercapacitors.[1-3] In this presentation it will be shown that flexible nanocellulose and polypyrrole composites, manufactured by chemical polymerization of e.g. pyrrole on a nanocellulose substrate, can be used as electrodes in charge storage devices containing either water or organic solvent based electrolytes. The aqueous flexible paper-based devices exhibit high charge storage capacities (e.g. 9 Wh/kg) as well as excellent power capabilities (e.g. 3.5 kW/kg) due to the large surface area (up to 250 m²/g) of the nanocellulose and the thin (i.e. 50 nm) layer of polypyrrole present on the nanocellulose fibers. The straightforward (paper-making) composite synthesis approach and the electrochemical properties of the resulting composites will be discussed. It will also be shown that high active mass paper electrodes [4-8] with mass loadings of up to 20 mg/cm² can be employed at high current densities without significant loss of electrochemical performance as a result of the advantageous structure of the electrodes. Devices with unprecedented areal and volumetric cell capacitances (e.g. 5.7 F/cm² and 240 F/cm³) that can cycle for thousands of cycles in aqueous electrolytes can likewise be realized. As the cellulose composites also can be also be used in lithium-ion batteries [9,10], functional (e.g. redox-active) separators [11] for lithium based batteries and in the realization of all-cellulose energy storage devices [12], the present materials provide new exciting possibilities for the development of green and foldable devices for a range of new applications, many of which are incompatible with conventional batteries and supercapacitors.


8:30 AM **ES03.06.02 Extreme Environments for Electrochemical Energy Storage Materials—Inspiration Gained from Implantable Medical Devices**
Amy C. Marschik, Kenneth Takeuchi and Esther S. Takeuchi; Stony Brook University, Stony Brook, New York, United States.

Implantable biomedical applications represent demanding operating environments for electrochemical energy storage materials and systems providing a unique set of challenges for successful design and implementation of such devices. While the capacity and power requirements can vary significantly depending on the specific application, several common challenges become evident. Volumetric rather than gravimetric density is the key consideration. The power source must operate effectively under elevated operating temperature. Reliable function under varied use conditions is essential. Long lifetimes as well as predictive state of charge indicators are essential. Advanced interrogation methods, particularly in-situ and operando approaches, can provide important mechanistic information to elucidate the behavior of the energy storage material. However, it is challenging yet important to design experiments which interrogate the system under application relevant conditions. Progress in investigation of energy storage materials for biomedical applications will be highlighted in this presentation, providing inspiration for design of new electrochemical energy storage solutions for a broad array of demanding applications.

9:00 AM **ES03.06.03 Strain Regulation of Editable Devices for Stretchable Supercapacitors**
Zhisheng Ly and Xiaodong Chen; Nanyang Technological University, Singapore, Singapore.

The ever-growing demands for stretchable electronics in applications of electronic textiles, electronic skins, and wearable health monitors, require concerted stretchability in energy storage devices. As one of the main energy supplies for stretchable and wearable electronics, stretchable supercapacitors are drawing increasing attention in recent years owing to their superior power density and long calendar life under deformation. Although some progress has been made on stretchable supercapacitors, traditional stretchable supercapacitors fabricated by predesigning structured electrodes for device assembling still lack the device-level editability and programmability. To adapt to wearable electronics with arbitrary configurations, it is highly desirable to develop editable supercapacitors that can be directly transferred into customizable shapes and stretchable structure according to application scenarios. Herein, we proposed an editable strategy to fabricate stretchable supercapacitors for regulation of the strain on the electrodes. The editable supercapacitors with customizable structures can regulate the peak strain of the electrodes below the fracture of the electrode materials, which enables a wider range of electrode materials for stretchable supercapacitors. The mechanically reinforced flexible electrode materials for the editable supercapacitors further guarantee the editable process and improve the mechanical stability of customizable devices. Editable supercapacitors for customizable shapes and stretchability using electrodes based on mechanically strengthened ultralight MnO₂ nanowire composites are developed. A supercapacitor edited with honeycomb-like structure shows a specific capacitance of 227.2 mF cm⁻² and can be stretched up to 500% without degradation of electrochemical performance. Taking advantages of these superior properties, the editable supercapacitors are integrated with a strain sensor, and the system exhibits a stable sensing performance even under arm swing. Besides, based on flexible porous polypyrrole composite electrodes, the supercapacitor arrays rearranged into an
expandable honeycomb structure can be further used to fabricate three-dimensional (3D) stretchable supercapacitors with customizable 3D shapes and enhanced areal energy storage performance. Being highly stretchable, easily programmable, as well as connectable in series and parallel, the stretchable supercapacitor with customizable stretchability and shapes is promising to produce efficient energy storage devices to power various portable, stretchable, and wearable devices. Our efficient design strategy provides a new design platform for the electrode materials in the customizable and stretchable electrochemical energy storage devices. Based on it, many other new methods and stretchable electronics could be further developed.

9:15 AM ES03.06.04 Ultra-Extendable Supercapacitors Consisting of Plied and Supercoiled Fibers Changsoon Choi; DGIST, Daegu, Korea (the Republic of).

The demand of stretchable electrochemical energy storage devices that can operate under extreme environments are growing in various aspects of the society requirements. Here, we report on fiber based highly stretchable supercapacitors comprising of nine supercoiled fiber electrodes and quasi-solid-state electrolyte. Each supercoiled fiber was fabricated by inserting a giant twist to supercoiling (coiling of a coiled fiber) a spandex fiber that is helically wrapped by forest-drawn carbon nanotube sheets. Plying these supercoiled fibers enables lower internal resistance, thereby resulting in improved rate-capability (54% retention of maximum capacitance at 1000mV/s scan rate) as well as high areal capacitance (4.23 mF/cm²). Moreover, the nine plied, supercoiled fiber based supercapacitors exhibited ultra-high stretchability in tensile direction (ε = 600%), while conserving 93% of initial capacitance during the reversible stretching. The new structured supercapacitors are posed for energy storage system with special electrochemical and mechanical properties that can work in extreme environments.

9:30 AM ES03.06.05 mm-Thick Soft Hybrid Scaffolds Enabling Wearable Supercapacitors with Ultra-High Energy and Power Densities Jian Shang and Zijian Zheng; Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, China.

The increasing power and energy demand for wearable electronics greatly stimulates the development of wearable energy storage devices with excellent flexibility, robust mechanical property and outstanding energy density. To power the wearable devices in a safe and cost-effective way, fabric-based flexible SCs have attracted intensive attention in both academical and industrial fields due to its significantly mechanical property and inherently safety. However, one major limiting factor regarding the practical application of fabric-based flexible SCs is insufficient areal energy density. The average areal energy density of wearable SCs is only in the range of 0.01 ~ 0.1 mWh cm⁻², which requires hundreds to thousands of square centimeters of SCs to powerly common used wearable devices, such as LED garments, wearable medical care devices and flexible displays.

Therefore, considering the limited surface area of a human body (~ 2 m²), the tremendous challenge for powering future wearable electronics lies on rational fabric-based flexible SCs design for robust areal energy density with prominent wear-ability properties, such as flexible, tailorable, waterproof and fire-retardant.

In this study, we report a new electrochemical fabrication preparation method to fabricate thick and high mass-loading hybrid electrode with superior conductivity and excellent ion diffusion property through successively filtering fresh mixture 1D core-shell pseudo-type materials and 2D rHGO nanosheets on carbon cloth to form a 3D soft hybrid scaffold. By using the afore-mentioned electrode fabrication method, we herein demonstrate the preparation of soft 3D scaffold electrodes with controllable mass loading, increasing from 5 mg cm⁻² to more than 30 mg cm⁻². After cathode and anode pairing and simple vacuum encapsulation, we assemble the 3D soft hybrid scaffold-like electrodes into all-solid-state flexible SCs with ultrahigh mass loading of 68 mg cm⁻² and thickness of 1.05 mm, which delivers a remarkable areal energy density of 1.05 mWh cm⁻² at a power density of 17.07mW cm⁻², along with high electrochemical life (91% retention after 3000 charge/discharge cycles). More importantly, the hybrid 3D scaffolds SC shows outstanding wear-ability properties: excellent mechanical flexibility (only 25% capacitive decay after 4000 bending tests), water-proof property (negligible capacitive decay after immersing in 20 cm deep water for 48 hours), fire-retardant ability (non-combustion-supporting even under butane flame thrower for 34 s) and tailor-abilities, which are critical for wearable applications.

9:45 AM BREAK

10:15 AM *ES03.06.06 UV-Cured Gel Polymer Electrolytes for Advanced Aqueous Li-Ion Batteries Konstantinos Gerasopoulos; Research and Exploratory Development Department, Johns Hopkins University, Laurel, Maryland, United States.

Li-ion batteries are the energy storage source of choice for rechargeable electronics applications due to their high energy density and long cycle life. Despite these benefits, Li-ion batteries suffer from safety concerns associated with the flammable organic solvents that are needed to maintain the high voltage window in the electrolyte. Water emerges as a natural, inherently safe alternative solvent. Its low electrochemical stability window of ~1.23 V limits the available energy density and cycle life of aqueous Li-ion batteries. Recent innovations in aqueous Li-ion batteries have introduced a new class of aqueous electrolytes termed as “water-in-salt” (WiS). In WiS electrolytes, a highly concentrated salt (>21 m) such as LiTFSI is typically used in water. At such high concentrations, water is bound and its electrochemical activity for gas generation is suppressed, extending the electrochemical stability to > 3.0 V.

In this work, significant advancements in WiS electrolytes are discussed, specifically through the incorporation of the WiS in a polymer matrix. When the liquid WiS is combined with a polymer, the need for a separator is eliminated and new form factors with minimal packaging can be realized. Using a high molecular weight polyvinyl alcohol (PVA)-based Gel Polymer Electrolyte (GPE) containing water-in-bisalt (WiBS), a flexible symmetric cell with LiVOPO₄F anode/cathode was built. This cell exhibited long cycle life (4000 cycles) at a 20C rate and continued to operate even after sustaining mechanical damage, such as cutting and exposure to air, immersion in salt water, and subjection to ballistic impact. The GPE properties can be dramatically enhanced when the high molecular weight polymers are replaced by UV cured acrylates. Using a combination of various acrylate monomers, cross-linkers, and photoinitiators, aqueous UV cured GPEs can be fabricated in fully aerobic/ambient conditions in less than 10 minutes with excellent control over thickness and mechanical properties. In addition to simplifying manufacturing, this approach significantly improves electrochemical performance as the UV cured GPEs exhibit an expanded electrochemical stability window (5.0 V) while maintaining ionic conductivity >1 mS/cm and enabled the use of Li₂Ti₃O₁₂ (LTO) as an anode. To further increase cycle stability and Coulombic efficiency, the UV cured GPE can be combined with a dry polymer electrode passivation. This passivation layer, which can be cast or UV cured, further suppresses hydrogen evolution on the anode and expands the stability of LTO-based cells to > 200 cycles at 2C rate. This UV cured passivation concept can be combined with previously demonstrated passivation strategies on graphite to extend the cyclic stability of “4.0 V aqueous Li-ion batteries” to >100 cycles. Finally, in addition to its use in the GPE and passivation layers, acrylate chemistry can also be used to replace the PVDF binder that is typically used in Li-ion batteries. Using a novel cross-linking approach, acrylate binders can be incorporated in battery electrodes with loadings as high as 90%, exhibiting comparable performance to those made with PVDF.

10:45 AM *ES03.06.07 Li-Ion Capacitors with Long Cycle Life and Wide Temperature Range for Military and Space Applications Jim P. Zheng; Electrical and Computer Engineering, Florida State University, Tallahassee, Florida, United States.

As a new generation of supercapacitor, the Li-ion capacitor (LIC) is an advanced energy storage device which consists of an electric double-layer capacitor (EDLC) cathode and a pre-lithiated anode [1], between which the ions shuttle during charge and discharge processes. Because of using pre-lithiated and low surface anode materials, the LIC can be charged to a maximum voltage as high as 4.0 V, which is much higher than that of traditional EDLC. The LIC cell not only retains all the advantages of EDLC such as high specific power (>10 kW/kg and long cycle life >100,000 cycles), but also exhibits a higher specific energy of 15-22 Wh/kg and a higher maximum cell voltage than that of the EDLC [2].

In addition to high specific power and long cycle life, we have also developed new electrolytes for LICs and compared performance of the LICs at various temperatures from 70 to -60 °C. The effects of charging temperature and negative electrode material on the low temperature performance of LICs are also studied [3].

Because of electrodes’ potentials of LIC are comparable to that of Li-ion batteries (LIBs), it allows the LIC and LIB to be assembled in one package as a LIB/LIC hybrid energy storage cell. In this talk, we will also demonstrate a new hybrid energy storage source which combines LIC and LIB. The fundamental difference between the proposed hybrid energy storage supercapacitor and the previous hybrid device (LIC) is that the new hybrid energy storage technology integrates two separate energy storage devices into one by synergistically combining battery and capacitor materials together to form positive (or cathode) and negative (or anode) composite electrodes, and it is rightly named as the “Internal Hybrid” energy source. This new hybrid energy storage device will not require any electric circuits for charge balancing and control. The overall internal hybrid system will be simple, light, compact, and cost effective when compared with the conventional (external) hybrid energy storage source.

Li-ion capacitors (LICs) and Hybrid LICs (H-LICs) are hybrid battery-capacitor energy storage devices that have been proposed as suitable alternative high-power power source technologies for operation in extreme environments with prolonged cycle-life performance. The LICs can accommodate both the non-faradaic (i.e., ion adsorption/desorption) and the faradaic (i.e., Li-ion insertion/extraction) processes of electrochemical double-layer capacitors (EDLCs) and lithium-ion batteries (LIBs) at the same time, respectively. The advantages of the hybrid LIC device includes higher power density and longer cycle life than a LIB and higher energy density than an EDLC. Recently, hybrid composite cathodes that combine capacitor and battery materials have shown promise for enhanced energy/power performance and extended life-cycle. The LICs were assembled as three-layered pouch cells in an asymmetric configuration employing Faradaic pre-lithiated hard carbon anodes and non-Faradaic ion adsorption-desorption activated carbon (AC) cathodes for LICs and lithium iron phosphate (LiFePO₄-LFP)/AC composite cathodes for H-LICs. The room temperature rate performance was evaluated after the initial LIC and H-LIC cell formation as a function of the electrolyte additives. The capacity retention was measured after charging at high temperature conditions, while the design factor explored was electrolyte additive formulation, with a focus on their stability.

References:
Recently, calcium-ion batteries (CIBs) have received attention as one of the post LIBs. The abundance of calcium resources can make CIBs cost effective. Calcium has a standard reduction potential of 0.17 V above lithium ($E^\circ = -2.869$ V vs. SHE for Ca/Ca$^{2+}$) that makes CIBs capable of a higher energy density compared to other multivalent ions such as magnesium, aluminum, and zine. In addition, calcium ion has a lower charge density than other multivalent ions, which may lead to relatively faster diffusion in a host material. 

Recently, Palacin et al. reported the feasibility of calcium plating and stripping using conventional organic electrolytes at elevated temperatures. To use calcium metal as a negative electrode in a cell, suitable cathode materials that store calcium ions are required. However, only a few cathode materials are reported so far to show electrochemical activity in calcium-containing electrolytes, such as V$_2$O$_5$, CaCo$_2$O$_4$, WO$_3$, and Prussian-blue analogues. 

In this presentation, some exploratory experimental results of electrochemical intercalation chemistry of divalent calcium ions will be presented with several host materials in aqueous electrolytes as well as non-aqueous electrolytes.


2:15 PM ES03.07.03
**Sb$_2$Te$_3$/CNT Composite Anodes for High Performance Sodium Ion Full Cells with Exceptional Energy and Power Densities**

Muhammad Ihsan Ul Haq, Jiang Cui, Baoling Huang and Jang-Kyo Kim; Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, Hong Kong.

Sodium ion batteries (SIBs) are an ideal alternative to lithium ion batteries for grid-level energy storage systems due to the low cost and abundance of Na precursors. The elements, such as SnO$_2$, Sb$_2$S$_3$, and SnS$_2$, undergoing the conversion and alloying reactions with Na hold great promise for high energy density SIBs. However, their large volume changes and low electrical conductivities lead to poor electrochemical performance and sluggish sodiation kinetics. In this work, we report the Na storage performance of a 3D topological insulator (TI), Sb$_2$Te$_3$ phase, and its composites with carbon nanotubes (CNTs) synthesized through a facile, low cost and scalable high-energy ball-milling (HEBM) approach. The composite electrodes exhibit an excellent reversible gravimetric and volumetric capacities of 422 mAh g$^{-1}$ and 1232 mA h cm$^{-3}$, respectively, at a current density of 100 mA g$^{-1}$ with ~97.5% capacity retention after 300 cycles. The roles of HEBM to introduce the Sb-C, Te-C, Sb-O-C and Te-O-C chemical bonds between Sb, Te and functional groups on CNTs are elucidated by combined XPS characterization and the first-principles calculations. Ex-situ TEM analysis reveals the formation of Na$_2$Te and Na$_2$Sb phases after the first sodiation, which are re-combined into Sb$_2$Te$_3$ after the first desodiation, supporting the reversible phase transitions in the composite electrodes. For practical application, the electrochemical performance of a sodium ion full cell (SIFC) consisting of an Sb$_2$Te$_3$/CNT anode and a Na$_3$V$_2$(PO$_4$)$_3$F$_2$ cathode is evaluated. The SIFC delivers a remarkable energy density of ~229 Wh kg$^{-1}$ at 0.5 C and excellent cyclic stability of more than 71% and 66% capacity retention at 5 C and 10 C, respectively, after 200 cycles. Even after fully charged at 40 C in 90 seconds, the SIFC presents an ultrahigh power density of 5384 W kg$^{-1}$. These findings may shed new insight into exploring the unique class of TI quantum materials as anodes for high performance SIFCs.

**References**


**SYMPOSIUM ES04**

**Solid-State Electrochemical Energy Storage**

**April 23 - April 26, 2019**

**Symposium Organizers**

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SESSION ES04.01: Solid-State Electrolytes I

**Session Chairs:** Donald Siegel and Wolfgang Zeier

**Tuesday Morning, April 23, 2019**

PCC North, 100 Level, Room 122 A

10:30 AM *ES04.01.01*

**Developments of Lithium-Ion Conductors with the LGPS Type for All-Solid-State Batteries**

Ryoji Kanno, Masashi Hori, Kota Suzuki and Masaaki Hirayama; Tokyo Institute of Technology, Yokohama, Japan.

The all-solid-state lithium battery offers an attractive option owing to their potential in improving the safety and achieving both high power and high energy densities. Among the lithium ion conductors proposed for the solid electrolytes, the sulphide LGPS (Li$_x$(GeP$_2$)$_2$) type system is a candidate because of its extreme high bulk ionic conductivity of over 10$^{-5}$ S cm$^{-1}$ at room temperature. To provide the electrolytes suitable for practical usage of the solid-state battery, electrochemical and chemical stabilities are important parameters besides the ionic conductivity. Composition variety of the LGPS type materials provide suitable combinations of the electrodes and the electrolyte. By the host compositions of Li$_x$(GeP$_2$)$_2$, various cation and anion substitutions were examined, and their structures, conduction mechanism and chemical/electrochemical stability will be discussed.

11:00 AM *ES04.01.02*

**Key Parameters for Solid Electrolytes—Learnings from Beta-Alumina and Future Opportunities**

M. Stanley Whittingham; State University of New York at Binghamton, Binghamton, New York, United States.

In the period 1967-1975, substituted beta aluminas [MAl$_2$O$_4$] were the subject of extensive study. These studies identified several key parameters that control the ionic conductivity of such ions as Na$^+$, Ag$^+$, Cu$^+$, Li$^+$, K$^+$, and NO$_3^-$ These parameters include the ionic size, the lattice spacing (diffusion path size), the defect concentration, defect type and diffusion mechanism. Later, similar studies on the WO$_3$, MoO$_3$, TiO$_2$ and VOPO$_4$ materials, all of which exist in several different structures with varying molar volumes, show the criticality of matching the diffusion path size to the mobile cation. The learnings from these studies will be described.
Solid state batteries with alkali metal anodes promise to deliver higher energy densities than conventional Li-ion batteries. However, alkali metal dendrite growth, even at modest rates and even when paired with dense, well-sintered solid electrolytes, leads to short circuits and cell failure. We have investigated the effect of cycling conditions on the formation of dendrites under controlled applied pressure. The results reveal the significance of plating/stripping current densities on cell failure. These results and their implications for the operation of a failure free all-solid-state battery will be discussed.

Cooperative Ion Migration in Li-Ion Conducting Glasses
Donald Siegel and Jeffrey Smith; University of Michigan, Ann Arbor, Michigan, United States.

Sulfur-based glasses have reemerged as promising candidates for use as solid electrolytes in Li-based batteries. Nevertheless, due to their amorphous structure, the ion migration mechanisms that underlie their high Li-ion conductivity remain poorly understood. The present study employs ab initio molecular dynamics to reveal the local structure and migration mechanisms in the prototypical Li-ion conducting glass, 0.75 Li$_2$S - 0.25 P$_2$S$_5$. A computational model of the amorphous structure was generated, and is shown to closely match the measured neutron weighted pair distribution. The structure data indicates that Li-ions experience a range of coordination environments, with typical Li-S coordination numbers between 3 to 5. Lithium is observed to migrate via correlated, 'string-like' events involving multiple adjacent cations. Furthermore, these migration events involve the dynamic participation of the PS$_4$ions, which undergo simultaneous rotation and translational displacements. This behavior contrasts with that of the Li$_2$PS$_5$crystalline analogue, were rotations and translations of the anions during migration events are severely limited. These observations provide direct evidence of the importance of anion dynamics on cation mobility in fast ion conductors.

Simultaneous Topographical and Electrochemical Mapping Using Scanning Ion Conductance Microscopy – Scanning Electrochemical Micoscopy (SICM-SECM)
Wening Shi, Gabriela Mendoza, Byong Kim and Keibock Lee; Park Systems, Santa Clara, Mexico.

Since the inception of scanning tunneling microscopy [1], electrochemists have sought to take advantage of scanned probe microscopy techniques to manipulate the spatial position of a probe with high resolution to facilitate simultaneous high resolution topographical, conductometric, and amperometric/voltammetric imaging of surface and interfaces. Lately, scanning ion conductance microscopy (SICM) [2], has emerged as a versatile non-contact imaging tool and been employed for a variety of applications. SICM has been used to investigate the surface topography of both synthetic and biological membranes, ion transport through porous materials, dynamic properties of living cells, and suspended artificial black lipid membranes. In addition, integration of complementary techniques with SICM has led to many exciting new applications, including scanning near-field optical microscopy and patch-clamping [3]. Powerful as it is, SICM remains insensitive to electrochemical properties, or, in other word, SICM is inherently chemically-blind and has no chemical specificity.

To obtain spatially-resolved electrochemical information, scanning electrochemical microscopy (SECM), also known as the chemical microscope, has been developed. SECM has been widely employed to examine localized electrochemical properties and reactivity of various materials/interfaces, such as electrode surfaces and interfaces, membranes [4], and biological systems. Despite its many applications, SECM, however, lacks reliable probe-sample distance control, and the probe is usually kept at a constant height during conventional SICM scanning. As a result, any variation in surface topography will result in changes in probe-sample distance, and thus leading to convolution to the measured faradaic current, which will complicate the subsequent data interpretation [4]. To address the above-mentioned issues for SICM and SECM, hybrid SICM-SECM techniques have been developed, in which the SICM compartment provides the accurate probe-sample distance control, while the SECM compartment measures the faradaic current for electrochemical information collection.

In this work, we demonstrate the use of an AFM (Park NX10) in combination with an ammeter for concurrent topography imaging and electrochemical mapping. The SICM-SECM probe utilized here consisted of a Au crescent electrode (AuE) on the peripheral of a nanopipette. High resolution probe-substrate distance control was obtained by the ion current feedback from SICM, while simultaneous electrochemical signal collection was achieved via the AuE from SECM. As a proof-of-concept experiment, a Au/Pyre pattern standard sample was imaged with the SICM-SECM technique. The Au bar and the Pyrex substrate were clearly resolved from the SICM topography image, with the bar height and pitch width closely matching the actual values. In terms of the electrochemical property mapping, higher Faradaic current was seen when the probe was scanned over Au bar as a result of redox cycling, while lower Faradaic current was observed when the probe was over the Pyrex substrate due to hindered diffusion. The capability of the SICM-SECM technique described here holds promise of many exciting applications in the field of electrochemistry, material science and battery research.


Raman Crystallography of Superionic AgI Reveals a Connection Between Anharmonicity and Ionic Conductivity
Thomas M. Brennessl1, Christian Gehrmann2, Arun K. Sagotra3, Claudio Cazorla4, David A. Egger5 and Omer Yaffe1; 1Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel; 2Institute of Theoretical Physics, Universität Regensburg, Regensburg, Germany; 3School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Basic understanding of ionic conductivity is critical to the development of new and technologically strategic solid electrolytes. Ionic conduction is fundamentally rooted in transforming vibrational thermal energy into diffusive atomic motion. While methods such as molecular dynamics (MD) can simulate the process accurately computationally, understanding of the process remains rooted in models employing either a harmonic vibrational or quasi-liquid model of the mobile ion. We propose to develop a model of ionic conductivity through the lens of anharmonic lattice dynamics. As a prototypical case we consider superionic AgI, with Ag conductivity > 1 S/cm at 150°C and activation energy of ~0.1 eV. While the Raman spectrum of this material has been studied for decades, using Raman crystallography at low wavenumbers we reveal a novel picture of vibrational motion in superionic AgI: The Raman spectrum in the superionic phase at 170°C is dominated by two first-order modes of symmetry E$_g$ and T$_{2g}$ and a central peak arising from motion with no restoring force. The mode symmetries confirm the accepted structural model of Ag occupying tetrahedral sites and indicate that mobile Ag participates in these modes. The very low phonon lifetimes (~100 fs) of the observed modes and pronounced central peak indicate the presence of strong anharmonicity. The vibrational power spectrum from MD simulations indicates that Ag motion contributes strongly to the observed central peak, and that both I and Ag display strong motion at the frequencies of the observed modes. From these results we hypothesize that anharmonic nuclear motion of both the mobile ion and host lattice is an important factor in ionic conductivity, and possible mechanisms will be discussed.

Mesoscopic Modeling of Microstructural Effects on the Effective Ionic Diffusivity of Solid Electrolytes for All-Solid-State Li Batteries
Tae Wook Heo1, Bo Wang2, Andrew Grieder3, Nicole Adelstein2 and Brandon Wood2; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2The Pennsylvania State University, University Park, Pennsylvania, United States; 3San Francisco State University, San Francisco, California, United States.
The ion transport kinetics in solid electrolytes is believed to be highly sensitive to the topological characteristics of ion conduction pathways. The conduction mechanisms usually involve concurrent ionic diffusion along a variety of mesoscopic features of internal microstructures such as bulk grain, structural domains, and associated boundaries as well as their network. In addition, inhomogeneous elastic interactions within the electrolyte microstructures are non-trivially coupled with ionic diffusion mechanisms. Due to the complexity of these structural features of the solid electrolytes during operation, it is significantly challenging to experimentally characterize the microstructure-ionic diffusion property relationship for better mechanistic understanding of relevant conduction mechanisms, it is necessary to thoroughly explore the impacts of individual microstructural factors on the overall kinetic properties and performances. In this talk, we will present our development of an efficient mesoscopic computational method for extracting the effective diffusivity of the solid electrolyte containing arbitrarily distributed microstructural inhomogeneities (e.g., differently oriented multiple grains, several structural variants of phase domains, and grain/domain boundaries) and their elastic interactions with Li conduction. Using three-dimensional digital microstructures generated by phase-field simulations as well as the fundamental diffusivity tensors of reference phases and boundaries derived from atomistic calculations as inputs, the developed method enables us to efficiently compute the effective ionic diffusivity tensor of the entire system. We will then discuss the applications of this framework to investigating the relationship between relevant individual microstructural features and effective diffusivity of highly conductive solid electrolytes (e.g., LLTO and LLZO) focusing on the impacts of topological features of grains, internal mesoscopic structures of high- and low-temperature phase domains, and grain phase boundary networks.

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

2:45 PM BREAK

3:15 PM ES04.02.05 Toward Room Temperature Solid State Fluoride Ion Batteries Ani Reddy Munnangi1, Irshad Mohammad1,2 and Maximilian Fichtner1; Helmholtz Institute Ulm (HIU), Ulm, Germany; Tallinn University of Technology, Tallinn, Estonia.

Lithium is an ideal metal to build high energy density batteries owing to its elemental properties. Lithium is highly electropositive (-3.04 V vs SHE), lightweight, monovalent and small ionic radius consequently it possesses high charge density and high mobility. On the other hand, fluorine is highly electromotive (+2.84 V vs SHE), relatively low weight, small in size and monovalent, high charge density and mobility is similar to lithium ions. However, fluorine is a corrosive and toxic gas, which forbid it as one of the electrodes. Nevertheless, fluoride ions can be transported between a metal and a metal fluoride through a fluoride transporting electrolyte, and fluoride-ion batteries (FIB) can be realized [1]. FIB offers high specific energy, high density, thermal stability, and safety. Despite the advantages posed by the FIBs, several challenges need to be addressed to realize its full potential. We have been working on various aspects related to FIB with the aim of developing sustainable fluoride ion batteries [2-4]. So far rechargeable FIBs have been demonstrated only at an elevated temperature like 150 °C and above. Recently, for the first time, we demonstrate room-temperature (RT) rechargeable fluoride-ion batteries using BaSnF$_6$ as fluoride transporting solid electrolyte [5]. BaSnF$_6$ shows high fluoride conductivity (3.5 × 10$^{-6}$ S cm$^{-1}$), but limited electrochemical stability. To be compatible with BaSnF$_6$, we have utilized low electropositive Sn, Zn as anode materials. However, to enable cells with high operating potentials, the electrolyte should be compatible with highly electropositive metals (e.g., Mg, Ce). Towards this, we developed a new interlayer electrolyte that is compatible with highly electropositive metals like Ce and Mg [6]. Further, utilizing the interlayer electrolyte, we demonstrate the operation of first open high potential RT FIB.

References:

3:30 PM ES04.02.06 The Effect of La-Site Dopants on the Microstructure and Ionic Conductivity of the Garnet-Type Li$_{1-x}$M$_{x}$ZrO$_3$ (M=Sm, Dy, Gd, Er, Yb; x=0-0.1-0.1.0) Solid Electrolyte Musah Abdulai, Kamil Burak Dermenci and Servet Turan; Materials Science and Engineering, Eskisehir Technical University, Eskisehir, Turkey.

Solid-state electrolytes are attracting more interest in battery technology due to the recent safety issue brought by the liquid type electrolytes such as flammability, toxicity etc. In recent years, lithium lanthanum zirconium (LLZO) is one of the solid electrolytes which has received attention due to the presence of wide chemical stability window, stability with lithium metal and high ionic conductivity at room temperature. The LLZO has two crystal phase, the stable phase which is the tetragonal and the cubic phase, the unstable phase. The attainment of the cubic phase which has the highest ionic conductivity is challenging as it required higher sintering temperature and dopants. The stabilization of garnet-type LLZO solid-state electrolyte in a cubic phase with appropriate dopants has become essential since they reduced the sintering temperature, sintering time and improved lithium ion conductivity. However, not much data has been reported regarding the role of Lanthanide series elements at the La-site on cubic phase stabilization of LLZO. In the present work, a solid-state electrolyte for the composition Li$_{1-x}$M$_{x}$ZrO$_3$ (M=Sm$_y$, Dy$_{1-y}$Er$_{1-x}$Yb$_x$; x=0-1.0-8) has been synthesized through the solid-state method. High-quality oxide powders were prepared. A stoichiometric weighed quantities of the starting powders were ground and calcined at 1000°C for 10 hours. The calcined powders were pressed into pellets and cold isostatically pressed at 265 MPa. They are sintered in air at 1200°C for 12-18 H using powder bed method. A critical investigation carried out by X-ray powder diffraction and refinement analysis revealed the synthesis of pure cubic LLZO phase. The solubility content of selected ions decreased with smaller size ions. The densities measured by using the famous Archimedes method increases as the ionic content in the garnet framework increased. Pellets having relative densities ranging from 73 g/cm$^3$ to 98g/cm$^3$ out of the theoretical density of LLZO (5.1 g/cm$^3$) were produced. The lattice parameter determined by both the analytical and the refinement technique obey the so-called Vegard’s law. However, the Yb$^{3+}$ exhibits a marginal slope due to the shrinkage that occurred. The SEM images indicate the reduction of porous microstructure with an increase in ionic contents which is consistent with the measured density values. EDS analysis confirmed the presence of the mentioned ions at this content. Lastly, the smaller ionic radius ions were observed to produced higher ionic conductivity of the garnet-type solid electrolyte.

3:45 PM ES04.02.07 Correlation Between the Activation Energy and Pre-Exponential Factor in Solid-State Li-Ion Conductors Sokisela Muy1, John C. Bachman2 and Yang Shao-Horn1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Mechanical Engineering, California State University, Los Angeles, Los Angeles, California, United States.

The correlation between the pre-exponential factor and the activation energy in the Arrhenius equation, variously known as compensation law or Meyer-Neldel rule, is ubiquitous in almost all physical/chemical systems whose kinetic is thermally activated. In this talk, we focus specifically on the origin of Meyer-Neldel rule observed in solid-state Li-ion conductors by systematically investigating the ionic conductivity in the model system Li$_x$PO$_4$-Li$_{2-x}$VO$_3$-Li$_2$GeO$_3$. We found that the activation energies and pre-exponential factors exhibit a strong correlation as expected from Meyer-Neldel rule. However, the series of compound with and without partial lithium occupancy were shown to fall into two distinct lines with a similar evolution with melt temperature, entropy theory, we were able to relate the slope to the inverse of the energy scale associated with phonon in the systems and the intertest to the Gibbs free energy of defect formation. Compiled data of pre-exponential factor and activation energy for commonly studied Li-ion conductors shows that this correlation is very general, implying an unfavorable trade-off between high pre-exponential factor and low activation energy needed to achieve high ionic conductivity. Understanding the circumstances under which this correlation can be violated might provide a new opportunity to further increase the ionic conductivity in Li-ion conductors.

4:00 PM ES04.02.08 Strain-Induced Effect on Defect Formation in Cubic Li$_{1-x}$A$_x$La$_{2}$ZrO$_6$: Solid Electrolyte Ashkan Moradabadi1,2 and Payam Kaghazchi3; 1Physikalische und Theoretische Chemie, Freie Universität Berlin, Berlin, Germany; 2Material Science, Technical University of Darmstadt, Darmstadt, Germany.

Rate performance of all-solid-state batteries (ASSB) depends strongly on the structure of electrolyte/electrode interfaces.

Lattice-mismatch-induced interfacial strain is an important parameter to control conductivity and thereby the rate performance of ASSB. In the present study, we have investigated the defect chemistry in unstrained and strained Li$_8$Li$_2$Al$_{25}$La$_{25}$Zr$_{25}$O$_{121}$ (Al-LLZO) as a promising solid electrolyte. We employed Coulomb-energy analysis and density functional theory (DFT) calculations to find the most favorable structures. Thermodynamics of defects were applied to determine type and concentration of defects as functions of $\mu_\text{Li}$ and $\mu_\text{O}$.

We also used the "elastic dipole tensor" method to analytically describe the effect of applied strain on defects thermodynamics in an efficient way.

At first, all possible Li and Al arrangements in Al-LLZO were explored and the minimum energy structures of pristine and defective Al-LLZO were determined. Afterwards, the range of chemical potential of constituent elements where Al-LLZO is thermodynamically stable were specified. Defect formation energy plots show that in the oxygen rich limit, combination of charged Li vacancy and Li interstitial (a Frenkel-like pair) has the lowest defect formation energy. In the oxygen poor limit, however, combination of 2-Li vacancy ($V_\text{Li}$) and 1-O vacancy ($V_\text{O}$), a Schottky-like pair, has the lowest formation energy which is followed by the Frenkel-like pair of Li as well as charged La interstitial. The low formation energy of the Schottky defect is due to a strong interaction between $V_\text{Li}$ and $V_\text{O}$.

Interaction is also evident when lattice strain is applied to the system. The effect of lattice strain on charged O vacancy formation is more significant compared to charged 2-Li vacancies and this effect is opposite between these two cases. According to our findings, ionic conductivity can be enhanced by controlling lattice mismatch at electrolyte/electrode interfaces in ASSBs.

4:15 PM ES04.02.09
Solid-State Electrolytes with SiS$_2$ as a Glass Former

Ran Zhao, Guantai Hu, Steven J. Kmiec, Ryan Gebhardt and Steve Martin; Iowa State University, Ames, Iowa, United States.

The most widely studied sulfide-based solid electrolytes are P2S$_5$-Li$_2$S glasses and their analogs, which show conductivity as high as 10-3 S/cm. However, due to the volatility of P2S$_5$, the atmospheric pressure synthesis method of P2S$_5$-Li$_2$S was limited to the high energy plenary milling, as a result, scientists started to investigate the ionic conductive glasses based on SiS$_2$. In 1985, Kennedy et al. reported a variety of oxide-sulfide glasses in the systems Li$_2$S-SiS$_2$-Li$_x$MO$_{2-y}$ with high conductivity and stability against crystalization. However, to the best of our knowledge, none of the studies have investigated the critical current density and the cyclibility of the glass solid electrolyte material when cycling pure lithium metal, and those important properties of the SiS$_2$ based glasses as a solid electrolyte is still unknown.

In this work, we demonstrate three glasses systems with SiS$_2$ as a glass former. First, Li$_2$S-SiS$_2$-P$_2$S$_5$ glass system was synthesized by mechanical milling and the mix glass former effect was investigated, the material were characterized using XRD, Raman and NMR, and tested in symmetric cells with lithium metal as electrodes. Next, to improve the glass stability in contact with lithium, Li$_2$S-SiS$_2$-P$_{20}$S$_5$ was made and tested in symmetric cells for electrochemical impedance spectroscopy and cycling, to address the high solid-solid interfacial resistance and short-circuiting dendrite problems, we demonstrate a simple strategy to engineer the lithium-GSE interface by forming an in-situ interlayer via a heat treatment. Then, Li doped Li$_2$S-SiS$_2$-P$_{25}$S$_5$ was made and melt-quenching technique and superior electrochemical properties were observed. These results provide a promising group of glass with SiS$_2$ as glass former that can be applied to lithium metal battery and other energy storage application as solid-state electrolytes.


4:30 PM ES04.02.10

Ionic Conductivity and Short Range Order Structures of Sodium Oxy-Thio Phosphate Glasses

Steven J. Kmiec, Adriana Joyce, Ran Zhao and Steve Martin; Iowa State University, Ames, Iowa, United States.

Sodium thio-phosphate glasses exhibit extraordinary high ionic conductivities, and have received a lot of attention as potential electrolyte materials in solid state batteries. However due to the poor chemical and electrochemical stability of sulfide materials efforts have been made to improve these properties though the incorporation of oxygen. The short-range order (SRO) structure of glasses were characterized using FT-IR, Raman and $^{31}$P Magic Angle Spinning NMR (MAS NMR) spectroscopies to identify the role of oxygen in the glass structure. Evidence suggests that the addition of oxygen causes a disproportionation reaction to occur in the structure through the formation of mixed oxy-sulfide tetrahedra. These units allow for greater uptake of sodium ion to the system leading to a large change in the physical properties, most notably in ionic conductivity.

SESSION ES04.03: Solid-State Cell Integration and Architecture
Session Chairs: Liangbing (Bing) Hu and Y. Shirley Meng
Wednesday morning, April 24, 2019
PCC North, 100 Level, Room 122 A

8:00 AM ES04.03.01

All-Solid-State Lithium Metal Batteries Utilizing Solid Polymer Electrolytes

Lauri Imholt¹, Gunther Brunklau²,³, Jijiehs Nair¹, Johannes Knasctcheew¹, Isidora Cekic-Lashovic¹ and Martin Winter¹,²
¹Helmholtz-Institute Münster, Forschungszentrum Jülich GmbH, Münster, Germany; ²MEET Battery Research Center / Institute of Physical Chemistry, University of Münster, Münster, Germany.

All solid state batteries in principle allow for a reduction of the net weight and volume of the battery, greater energy output, and better ion transport while affording small self-discharge, minimal wear and tear, and a more uniform output voltage [1]. Materials that can reversibly store Li$^+$ to create capacity are potentially good anode materials, among which lithium offers a particularly high theoretical specific capacity, though lithium metal in contact with liquid electrolytes often leads to formation of high surface area metallic lithium structures upon repeated recharge and charge [2]. Solid electrolytes can be made compatible with lithium metal and allow to almost suppress lithium deposits rendering them a viable alternative, including advantages in terms of mechanical stability, operational safety and simplicity of cell design [3]. Solvent-free electrolytes require further improvement of achievable lithium ion conductivities at ambient temperatures, e.g. via design of nanostructures that facilitate directional pathways for Li$^+$ transport [4]. Polyoxotanate and ethylene oxide (EO) based polymeric electrolytes exhibiting impressive ionic conductivities and excellent oxidation stability at potentials higher than 5.5 V vs. Li/Li$^+$ will be discussed, highlighting interesting characteristics in terms of specific capacity, cycle life and Coulombic efficiency. In addition, Polysulfonamide based single ion conducting blend polymers that other than dual ion conducting electrolytes offer excellent transference numbers will be considered. The polymer blend electrolyte has superior oxidative stability and long-term stability against lithium metal, hence enabling operation in Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)$_2$O$_{2}$/lithium metal cells at 20 °C and 60 °C, respectively [5]. Moreover, considerable improvements of sulfidic-based ceramic electrolytes will be discussed in view of challenges associated with materials processing and reproducibility aspects, in this way providing a reasonable basis for systematic exploration of electrode/electrolyte interfaces.


Garnet-Based Advanced Solid-State Batteries

Liangbing (Bing) Hu; Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States.

I will start by giving an overview of active research activities in my research group located at University of Maryland Energy Research Center, including wood materials toward sustainability, 3000K high temperature materials and processing (Science 2018), wood nanotechnologies (Nature 2018), beyond-Li ion batteries (solid state, Na-ion). Then I will focus on our recent development on garnet-based solid-state Li-metal batteries including interface engineering to improve the wetting between Li metal anode and Garnet solid-state electrolyte (Nature Materials 2016; Advanced Materials 2017; Science Advances 2017); Garnet based 3D Li ion conductive framework (bilayer, triayer) toward high energy density Li-S batteries (EES 2017); Garnet nanofiber based flexible, hybrid electrolyte with a high Li ion conductivity (PNAS 2016), and in-situ neutron depth profiling technique in understanding Li-garnet and CNT-garnet interfaces (JACS 2016).

8:00 AM *ES04.03.02
Prospects and Challenges of Solid Electrolytes in Lithium Rechargeable Batteries

Ratnakumar V. Bugees, William C. West, Erik Brandon, Keith J. Billings and Simon C. Jones; Jet Propulsion Laboratory/Caltech, Pasadena, California, United States.

Solid electrolytes have been successfully developed for use in high temperature energy devices, e.g., Ytria stabilized zirconia (YSZ) as oxide ion conductors in solid oxide fuel cells operating at ~800°C, and sodium b-alumina solid electrolyte in Na-S and Na-Metal chloride (Zebra) batteries operating at 300-400°C. Excellent performance and lifetimes have been demonstrated in these devices. The b-alumina solid electrolyte separator enabled successful implementation of molten anode and cathodes in Na-S cells, and with a molten salt electrolyte for the Zebra batteries, without the issues of any (Na) dendrites during cycling. Development of room temperature Li-conducting solid electrolytes has been the topic of intense research in the last few years, mainly guided by the potential to replace the flammable organic electrolytes in current Li-ion cells for enhanced safety.

Additionally, these solid electrolytes can improve energy characteristics beyond the current Li-ion cells with the use of Li anode and high voltage cathodes. A noteworthy success was reported by Bates et al with a new solid electrolyte, LiPON (Lithium Phosphorus Oxynitride), which has a moderate ionic conductivity of 10^-4 S/cm at 25°C, but impressive interfacial stability against Li and cathodes. One difficulty with this material is its method of synthesis, i.e., reactive sputtering directly on cathode layers, which is not amenable for scale up. At JPL, we utilized this electrolyte in the development of micro-batteries with Li/LiCoO2 cells and demonstrated excellent cycle life at ambient temperatures and also at high temperature with cells fabricated by Front Edge Technologies.

The search for new Li-solid electrolytes has proceeded more rapidly in recent years, with improved conductivity of some of the recent systems, approaching and even surpassing that of liquid electrolytes. Room temperature conductivities of around 1 mS cm^-1 have been shown in lithium garnet oxides. These systems typically require co-sintering to obtain good contact between the electrode and electrolyte, which is important for battery performance. More recently, new sulfide superionic conducting materials have emerged with higher conductivities and with mechanical properties amenable for better physical contact with electrodes. These include Li2GeP2S6 (LGPS), with a conductivity of 12 mS/cm at 25°C, and Li2PSi11, a glass-ceramic with a conductivity of 27 mS/cm at 25°C. The challenges associated with these high conductivity solid electrolytes are: 1) Poor interfacial stability of almost all the solid electrolytes towards Li or cathode materials, which warrants intermediate buffering layers (e.g., Al2O3) and ii) Need to have sufficient solid electrolyte as part of cathode, i.e., composite cathode, for a good utilization of cathodes of nominal thickness. Often, a hybrid system is preferred, where the solid electrolyte is utilized to protect Li anode and is used in conjunction with a conventional liquid electrolyte. In this paper, we will review the status of this technology and also present the results of our studies on the interfacial stability of some of these solid electrolytes towards Li anode and various cathodes.

References:

9:00 AM *ES04.03.03
Wet Chemical Processing of Lithium Garnets—Previous Challenges, A New “Solution”

Zachary D. Hood1 and Jennifer L. Rupp1, 2, 3; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Lithium solid electrolytes are expected to improve next-generation energy storage technology on the basis of energy density, safety, cost, amongst other parameters. However, there has been limited success in growing oxide-based solid electrolytes, such as Li3xAlxLa2-xZr2O7 (LLZO), into thin films between 200 nm and 5 μm in thickness using scalable solution-based techniques. Several vacuum-based2 and sol-gel-derived3 methods have shown promise in making thin garnet-based solid electrolyte films with relatively high ionic conductivity (~10^-3 ~ 10^-4 Scm^-1 at room temperature), yet lithium loss during the post annealing can alter the phase as well as significantly affect the lithium ion conductivity. Only a recent report4 has overcome this issue by using an alternative ceramic processing strategy establishing lithium reservoirs directly in lithium garnet-based films (through LiN multilayers) that allow for lithiated and fast-conducting cubic solid state battery electrolytes at unusually low processing temperatures using pulsed laser deposition. Still, the exploration of scalable fabrication techniques is of special importance to develop thin films of garnet-based solid electrolytes with high ionic conductivity. Here, we present a new solution based on spray pyrolysis for growing garnet-based thin films. We show that the crystallization and the phase transformation can be modulated to lower temperatures (~750 °C) by tuning the concentration of cations and the boiling point of the solvents used in the spray solution. Also, by altering the chemistry of the spray solution and the post-annealing conditions, we show that the surface roughness can be modulated while still maintaining dense and continuous membranes of LLZO. Our results highlight a new opportunity for manufacturing garnet-based solid electrolytes with tunable electrochemical surface areas. The insights from this work are expected to serve as fundamental guidelines for future optimization toward solution-based processing of thin film superionic garnet-based materials for next-generation lithium metal batteries.

Acknowledgements:
This research was supported by Samsung Electronics and a portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

References:

9:45 AM BREAK

10:15 AM *ES04.03.05
Solid-State On-Chip Energy Storage Devices Based on Photopatternable Ionogel Solid Electrolytes

Christopher S. Choi1, Kevin Brousseau2, Patrice Simon1 and Bruce S. Dunn1; 1University of California, Los Angeles, Los Angeles, California, United States; 2Materials Science department - CIRIMAT, Université Paul Sabatier,, Toulouse, France.

While microfabrication techniques have been used extensively to form the complex circuitry of modern microelectronic devices, its application in the fabrication of electrochemical energy storage (EES) systems has not been considered traditionally. However, the microfabrication approach can open new routes for minimizing the dimensions...
of EES devices and for directly incorporating them with integrated circuits, sensors, MEMS devices, and various other Internet-of-Things components. In particular, the photopatterning of mechanically robust solid electrolytes offers several potential advantages, such as the spatial control with micron and sub-micron resolution in complex designs, ease of co-packaging with other integrated circuits, and high-throughput wafer-scale fabrication of EES arrays.

This presentation will review our work on the fabrication and characterization of a photopatterning, ionically conducting solid electrolyte. Electrolyte materials consist of the epoxy-based photopattenable polymer matrix that confines an ionic liquid, thus providing an appropriate source of ions and measureable ionic conductivity of 0.4 mS cm⁻¹. This ionogel solid electrolyte possesses excellent mechanical integrity, demonstrates good electrochemical stability, and can be photopatterned with micrometer-scale resolution. To validate its electrochemical performance and on-chip integration, fabrication of all-solid-state micro-supercapacitor devices was demonstrated using microfabrication methods that are fully compatible with current semiconductor processing. The interdigitated electrode designs were optimized to minimize the ion transport distance, compensating for the modest ionic conductivity of our solid electrolyte. The resulting TiC-derived-carbon micro-supercapacitor devices with 15-μm electrode spacings demonstrate a high areal capacitance and long-term electrochemical stability. In addition, the potential range and total capacitance of micro-supercapacitor devices can easily be tailored through modifying the device arrangements in series or parallel configurations.

10:45 AM *ES04.03.06
Thin Film Technology—Opening New Frontiers for 3D Solid-State Energy Storage Gary Rubloff, Keith Gregorczyk, David Stewart, Blake Nuwayhid, Angelique Jarry, Nam Kim, Jake Ballard and Sang Bok Lee; University of Maryland, College Park, Maryland, United States.

Solid state batteries (SSBs) can be fabricated using thin film processing techniques like those which dominate major high-tech markets such as semiconductors, displays and optoelectronics. In particular this approach - profoundly divergent from today’s Li ion battery mainstream - enables controlled patterning of electrode and electrolyte shapes and connectivity that opens the door to simultaneous high energy and high power, 3D nano/micro configurations exploiting conformal high aspect ratio geometries, and flexible form factors for integrating SSBs into multifunctional systems. We have made substantial progress in realizing these benefits in conformal 3D vertical interdigitated nanobattery arrays, forming SSB layers in high aspect ratio nano/micro pores, affording the opportunity to project performance. We are also pursuing a contrasting lateral design that promises similar benefits. We compare the vertical and lateral designs in terms of projected performance and associated synthesis and fabrication challenges, and we highlight key scientific challenges at the levels of nanoscale interfaces and mesoscale architectures.

11:15 AM ES04.03.07
Advanced Sulfide Solid Electrolyte and Battery Design for 5V Cathode Xin Li; Harvard University, Cambridge, Massachusetts, United States.

Ceramic sulfide solid electrolyte can show high lithium conductivity, while the voltage stability was reported as an issue in many previous literatures. We show in this talk a new way to improve the voltage stability of sulfide solid electrolyte materials by microstructure and battery designs. The improved battery performance and voltage stability are shown by electrochemical test. A combination of first principle simulation and transmission electron microscopy imaging techniques are used to understand the principle behind the phenomenon.

Specifically, sulfide Li-Si-P-S has been synthesized, characterized and tested to show an improved voltage stability window up to 3.1 V and quasi-stable voltage window up to 5V from a combined thermodynamic modeling and DFT simulation understanding the principle behind this promising result. A new design principle and theory is proposed and discussed systematically for tuning the voltage stability of solid electrolyte, giving the guidelines for the design of advanced sulfide electrolytes. All-solid-state battery using 5V cathode materials based on sulfide solid electrolyte is demonstrated in our experiment.

References: Advanced sulfide solid electrolyte by core-shell structural design, Nature Communications, (9), 4037 (2018)

11:30 AM ES04.03.08
Thin-Film Battery Architecture Approaches for High Power and Energy David M. Stewart, Blake Nuwayhid, Keith Gregorczyk, Angelique J. Jarry and Gary Rubloff; University of Maryland, College Park, Maryland, United States.

Producing battery materials by thin film deposition techniques provides many benefits for future solid state batteries (SSB) and opens up new possibilities for on chip energy storage in microelectronics applications operating in harsh environments and with high power demands. We have recently demonstrated that a fully 3D thin film based SSB can be produced by atomic layer deposition (ALD) into an array of nanopores etched into an inert substrate, with potential to scale capacity to rival that of modern lithium ion batteries. Such extreme 3D architectures apply certain constraints to the selection of materials and deposition techniques, and effectively limits us to using ALD, not to mention limiting the ways in which we wire these 3D TFSSB to the rest of the device.

Experiments on an alternative TFSSB architecture, simpler and more efficient in many regards, are presented which relaxes many of these constraints, while retaining the same capacity scaling performance. In this architecture, the battery layers are deposited in a planar way using magnetron sputtering, and the processing is repeated to produce multiple layers of TFSSB in the same space. Once electrode connections are completed, this multibattery architecture alleviates many of the concerns raised from the previous 3D battery, while presenting other issues (e.g., annealing steps required to produce the desirable phase in the cathode).

We will describe and compare our measurements on these two distinctly different approaches to 3D battery architectures for high power-energy solid state electrochemical energy storage, considering such aspects as mesoscale synthesis, performance scaling, flexibility in form factor, and integration into multifunctional systems.

SESSION ES04.04: Solid-State Battery Composite Constructs
Session Chairs: Jeff Sakamoto and Yoshitaka Tateyama
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 122 A

1:30 PM *ES04.04.01
Interfacial Engineering of Solid-State Batteries Using Atomic Layer Deposition Neil P. Dassargues; Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Solid-State batteries have experienced a recent explosion in research and development, owing to their potential to improve safety and enable higher energy density electrode chemistries. However, it has been widely recognized that all solid-state interfaces present unique challenges compared to traditional liquid electrolytes, including reduction of high interfacial impedances (which can evolve during cycling), accommodation of mechanical stresses due to solid-solid interfacial contact with active materials, and (electro)chemical instabilities that can arise from localized gradients in ionic and electronic concentrations.

To address these challenges, our group focuses on gaining new fundamental insights into the coupled phenomena occurring at interfaces, and applied this knowledge to rationally design interfacial chemistry to address the root cause of performance limitations. The key enabling technology that will be discussed in this talk for surface modification is Atomic Layer Deposition (ALD). This is a gas-phase deposition process capable of conformally coating high aspect-ratio structures with sub-nanometer control in thickness. This atomic-scale modification of surfaces allows for precise control of interactions at heterogeneous interfaces, including (electro)chemical stability, interfacial kinetics, wettability, and mechanical load transfer.

In this talk, examples will be presented in both bulk solid-state battery interfaces, and thin film electrolytes deposited by ALD. By studying interfacial chemistry across length
The advent of solid-state batteries has spawned a recent increase in interest in lithium conducting solid electrolytes, especially in the lithium thio phosphates. While current lithium electrolytes provide fast-ionic conduction to fundamentally study solid-state batteries, their ionic conductivities are not sufficient for thick electrode configurations, which will really allow high energy densities to be achieved. In this presentation, we show how an understanding of the structure-transport properties of the lithium argyrodites Li$_x$PS$_{4-x}$ can help tailor the ionic conductivity. We show that an anion site disorder between $S^2$ and $X$ is beneficial for the activation barrier and that an induction of the site disorder in Li$_x$PS$_{4-x}$ leads to a significant improvement of the conductivity. Having achieved the fastest lithium argyrodite so far with $\sim 18$ mS/cm, solid-state batteries with thick electrode configurations (150 – 350) can be built. Due to the optimized solid electrolyte, the solid-state battery can be cycled even at 1C with no capacity fade over 150 cycles. This work shows that optimizing solid electrolytes helps to achieve stable cycling at high rates in solid-state batteries with thick electrodes. Finally, we will show how tuning the lattice polarizability in ionic conductors affects the ionic transport due to a softening of the lattice. Our work shows that the idea of the “softer, the better” needs to be revisited. Lastly, we show how volume changes, induced by electrochemical (de-)intercalation, affect the performance in solid state batteries providing an understanding of the underlying mechanochemical influences in solid-state batteries.\(^{(1)}\) (1) Janek, J.; Zeier, W. G. A Solid Future for Battery Development. Nat. Energy 2016, 16141.


All solid-state batteries have become the focus of next-generation Li-ion battery research and development to meet the ever-growing demands on safe and high-energy-density storage systems. Replacing conventional electrolytes with solids mitigates issues associated with flammable organic liquid and makes safer battery systems. Solid electrolytes which are stable against lithium and resistant to Li dendrite penetration could enable the use of metallic lithium anode, offering a promising pathway to deliver lithium-ion cells with energy densities that significantly exceed 350 Wh/kg. While each main class of solid electrolytes has their intrinsic challenges, integrating different groups of solid electrolytes such as polymers and ceramics has the potential of bringing their individual advantages together and overcoming their drawbacks. In this study, we fabricated a group of hybrid polymer/ceramic electrolytes made from commercially available materials. Their ionic conductivity, electrochemical stability, interfacial stability towards metallic lithium, thermal property, processability and mechanical strength were systematically investigated. Finally, we develop a metrics to screen these hybrid solid electrolytes and identify promising candidates which are most relevant to electric vehicles (EV) applications. Our study illustrates the importance of component integration in developing high-performance solid-state electrolyte. This work serves as a guide to select the appropriate solid electrolytes that can power future electric vehicles.

4:45 PM ES04.04.07
Si Doped Flexible Self-Supporting Comb Like Polyethylene Glycol Copolymer (Si-PEG) Film as Polymer Electrolyte for All-Solid-State Lithium-Ion Battery

Dandan Li1,2 and Dean Shi1,2; 1Hubei University, Wuhan, China; 2Materials Science and Engineering, Hubei University, Wuhan, China.

Self-supporting comb like Si-PEG copolymer with flexible Si-O-C bonds in the main chain and pending short PEG chains as the side chain was synthesized to improve the low temperature performance and overcome the dilemma between good mechanical and electrochemical properties of polymer electrolyte in lithium ion battery. The tensile strength of Si-PEG polymer electrolytes (SPH15) is 0.8MPa at 30°C, which is strong enough to inhibit the growth of lithium dendrites. The ion conductivities of Si-PEG (SPH15) are 1.2×10-4 S/cm at 30°C and 3.2×10-7 S/cm at 10°C, respectively, which are one order higher than those for PEG based copolymer electrolytes without Si doping. Assembled LiFePO4/SPH15/Li half batteries can deliver specific capacities of 84 mAh/g at 10°C and present 75% capacity retention after 500 charge-discharge cycles at 0.5C.

ES04.05.01
Ionic Liquid Embedded Poly(methacrylate)-Comb-Copolymer Electrolytes for Solid-State Supercapacitor
Jadjun Lee and JongHak Kim, Yonsei University, Seoul, Korea (the Republic of).

We report a highly ionic conductive gel polymer electrolyte for supercapacitor, composed of poly[2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate]-poly(oxyethylene methacrylate) (PBE) copolymer and 1-Ethyl-3-methylimidazolium dicyanamide ionic liquid. When incorporated with EMIM DCA, selective interaction between ether groups and EMIM DCA induced micro-structured morphology, observed by (TEM). Structured morphology effectively suppressed aggregation of EMIM DCA and provide ion transport pathway, which led to fast diffusion of mobile ions. The PBE/EMIM DCA electrolytes showed gel-like morphology, which is suitable to fabricate solid-state, leakage-free supercapacitor. The best performance of supercapacitor using PBE/EMIM DCA electrolytes exhibited higher capacitance (125.1 F g-1) than that of reference PVA/H3PO4 electrolyte (39.5 F g-1) due to its high ionic conductivity and good affinity with electrode.

ES04.05.02
Stabilizing Lithium Electrodedeposition in Solid Polymer Electrolyte through Introducing Polymeric Ionic Liquid
Xiaowei Li and Christopher Li, Drexel University, Philadelphia, Pennsylvania, United States.

Development of practical high-energy-density lithium metal batteries (LMBs) remains a grand challenge due to uneven lithium deposition and uncontrollable lithium dendrite growth. Hence, to further stabilize lithium electrodeposition, polymeric ionic liquid (PIL), poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PDDA-TFSI) with TFSI- as the anions, is introduced in the cross-linked poly(ethylene glycol) (PEG) solid polymer electrolyte to form an interpenetrating polymer network (IPN) in order to homogenize the anion concentration and reduce the local space charge-associated large electric field during the electrolyte cycling. Galvanostatic cycling and polarization measurements of symmetrical lithium cells show that introducing proper amount of PIL could improve the lithium dendrite resistance at relatively low current density, and reduce anion depletion velocity and extend Sand’s time when polarized at high current density, indicating the improved lithium electrodeposition stability. Calculations from the Chazalviel model reveal that the improvement derives from elevated ionic conductivity and ionic concentration when PIL is introduced. The results demonstrated here represent a facile way for stabilizing lithium electrodeposition in high-performance LMBs.

References

ES04.05.03
Mixed Electronic and Ionic Conduction Properties of Reduced Lithium Lanthanum Titanate
Michael Wang and Jeff Sakamoto, University of Michigan, Ann Arbor, Michigan, United States.

Solid state electrolytes have garnered significant interest in recent years due to their potential to enable high energy-density Li-metal batteries. Because solid electrolytes have the potential to physically stabilize the Li-metal/electrolyte interface, significant emphasis has been placed on understanding the kinetics and stability of the Li/electrolyte interface. As significant progress is made in stabilizing the Li/electrolyte interface at higher current densities, there is an increasing need to develop and improve compatible cathodes for all solid-state architectures. Currently, achieving a combination of facile ion and electron transport through the cathode thickness is emerging as a challenge toward high-rate cycling. It has been proposed that a method of introducing charge transport in the cathode is introducing a mixed electronic and ionic conductor (MEIC) which can reduce the amount of net
conductive additive required. This study focuses on the perovskite Li_{12}La_{2/3}Zr_{12}O_{41} (LLTO) as a model MEIC system. The physical and charge transport properties for LLTO are measured in the oxidized and reduced state. Furthermore, the effects of P2O5 and grain size on the transport properties are examined. Overall, this work will motivate the further study and development of MEIC materials in the context of solid-state batteries and may improve the potential for high-rate cathodes for solid-state architectures.

ES04.05.05
A Novel De-Coupling Solid Polymer Electrolyte via Semi-Interpenetration Network for Lithium Metal Battery Yongwei Zheng, Xiaowei Li and Christopher Li; Drexel University, Philadelphia, Pennsylvania, United States.

Solid-state lithium metal battery attracts lots of interest for its high theoretical capacity and less flammability. Poly (ethylene oxide)-based solid polymer electrolyte (SPE) has been proved to be successful in lithium metal battery. However, the Li-ion transference number which restrains the battery working is at high current rate. Herein, a novel SPE combined poly (ethylene oxide) and poly (propylene carbonate) and with semi-interpenetration network structure is reported. The synthesis of the SPE is based on the crosslinking of octakis(3-glycidoxypropyldimethylsiloxyl) octasilsequioxane and amine-terminated polyethylene glycol while adding linear poly (propylene carbonate) with controlled concentration. The optimized SPE could be stably cycled for over 300 hours at current density of 1.5 mA cm−2 during the galvanostatic symmetrical cell plating/stripping experiment. Lithium ion transference number could reach 0.38 which is almost double to the single network SPE. Scanning electrical microscope (SEM) revealed that the involvement of poly (propylene carbonate) could effectively suppress the lithium dendrite growth. X-ray photoelectron spectrum (XPS) found Li plating/stripping experiment. Lithium ion transference number could reach 0.38 which is almost double to the single network SPE. Scanning electrical microscope (SEM) revealed that the involvement of poly (propylene carbonate) could effectively suppress the lithium dendrite growth. X-ray photoelectron spectrum (XPS) found Li.

ES04.05.06
Compositional Dependence of Structural, Thermal and Electrochemical Properties of Lithium Oxythio-Silicophosphate Glassy Solid-State Electrolytes Guantai Hu, Ran Zhao, Steven J. Kmiec, Ryan Gehbardt and Steve Martin; Iowa State University, Ames, Iowa, United States.

Hazards associated with the utilization of organic liquid electrolyte has created a growing concern while the number of lithium rechargeable battery (LRB) applications has been increasing over the last two decades. Glassy solid-state electrolytes (GSSEs) have been considered as a safer alternative credited to its promising thermal stability and physical durability. In addition to this, the elimination of fire and explosion risks provides the chance to adopt high-energy-density metallic lithium as anode material, leading to drastic improvements in overall energy density of LRBs. However, few papers have been reported on lithium oxythio-silicophosphate (LiPSiSO) GSSE, and the compositional dependence on structural, thermal and electrochemical properties are not clear yet.

In our research, LiPSiSO GSSE materials were synthesized via melt-quench method, and the structural and thermal properties were characterized using differential scanning calorimetry, Raman, infrared, nuclear magnetic resonance spectroscopies. The electrochemical properties have been tested via electrochemical impedance spectroscopy and direct-current cycling methods, for which powdered LiPSiSO GSSE was pressed into thin pellets (~1mm). The experimental results showed the structural, thermal and electrochemical properties of our GSSE are highly composition dependent. This insight allows for the correlation among those properties, and helps optimize the performance of LiPSiSO GSSEs by composition adjustment during synthesis.

ES04.05.07
Solid State Li-La-Zr-O2–Polymer Composite Electrolyte for All–Solid–State Lithium Batteries Parisa Bashiri1, Prasad Rao Talakonda1, Vaman Naik2 and G. Abbas Nazri1,2; Wayne State University, Detroit, Michigan, United States; 1University of Michigan–Dearborn, Dearborn, Michigan, United States.

Current lithium-ion batteries contain flammable organic-based electrolyte with limited voltage stability. A promising solid state electrolyte has been proposed to improve safety and limited voltage stability of the current lithium-ion battery. A global research activity is underway to develop a safe solid-state electrolyte with high conductivity and high voltage stability to replace the organic liquid electrolyte.

The polymer-salt complex electrolytes have been investigated in the past. However, this class of electrolyte exhibits low ionic conductivity (10−6 – 10−7 S cm−1) at room temperature due to their high degree of crystallinity at low temperatures and a high degree of ion-pairing that limits salt solubility. These issues have been addressed by adding plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), etc., or using inorganic fillers. In this research, we have studied PEO based polymer electrolyte with inorganic filler, Li-La-Zr-O2 (LLZO), which is also a Li-ion conductor. We have shown that the ionic conductivity of PEO-LLO composite electrolyte increases by one order of magnitude upon adding LLZO (20 wt%) and EC (20 wt%) and lowering the activation energy from 0.6 eV to 0.4 eV with high (5V) voltage stability. The results of a detailed study of electrochemical properties of PEO-LLO composite electrolytes using electrochemical impedance spectroscopy, linear sweep voltammetry, and chronoamperometry will be presented.

ES04.05.08
High-Capacity Slurry-Coated Sheet-Style Tin Anodes for All-Solid-State Lithium-Ion Batteries Nathan A. Dunlap; Mechanical Engineering, University of Colorado - Boulder, Boulder, Colorado, United States.

High capacity all-solid-state Li-ion battery anodes were prepared using an industrially scalable solution coating processes. Employing commercially available polyacrylonitrile as a mixed conducting binder, we have demonstrated stable cycling, high capacity electrodes with large mass loadings of tin active material. This is, to our knowledge, the first time a high capacity lithium-alloying material has been utilized in a slurry-coated sheet-style all-solid-state Li-ion battery anode. Optimization of this new electrode architecture resulted in a sheet-style anode capable of retaining an electrode specific capacity of 643.5 mAh g-1 after 100 charge-discharge cycles at a 0.1C rate. We believe that this work represents a step forward for slurry-coated electrodes and that the continued development of these high capacity sheet-style anodes will be critical to the commercialization of the all-solid-state Li-ion battery.

ES04.05.10
Atomic-Level Understanding of Thermal Management for Superionic Conductor Battery Materials Ming Hu; University of South Carolina, Columbia, South Carolina, United States.

The importance of clean and efficient energy storage has grown enormously over the past decades, driven primarily by concerns over global warming, diminishing fossil-fuel reserves, and increasing demand for portable electronics and grid storage systems. The performance of energy storage devices depends crucially on the properties of their component materials. Rechargeable lithium ion batteries (LIBs), due to their high energy density superior to all other secondary batteries, have become instrumental in powering nearly all of our small, portable electronics. However, LIBs have their drawbacks. One of the most pressing challenges for LIBs is overheating. During charging, a tendency for growth of small Li filaments, known as dendrites, occurs. The dendrites can short-circuit the cells and trigger a process known as thermal runaway, which can lead to violent overheating reactions. When a LIB overheats, the components inside are at risk of decomposing and undergoing a series of reactions that can generate even more heat and gaseous products. This will induce the liquid electrolyte that comprises organic chemicals to combust. In order to extend the battery life between charges and create a smaller, higher-energy battery, today’s LIBs have twice as much active material and tinier separators, setting the stage for a new generation of heat-triggered recalls. Despite many safety mechanisms have already been incorporated into batteries to prevent inadvertent charging and excessive current, there is little research focusing on exploring the fundamental mechanism of heat transport in LIBs in both stationary and charging conditions and how the excess heat is generated. In this work, by performing first-principles and molecular dynamics simulations, for the first time we give a robust and detailed explanation of the thermal transport mechanism in superionic material LiSi. At the temperature range in which the system can be regarded as a solid, the large hopping of Li is found to be responsible for phonon thermal conductivity’s deviation from the traditional 1/T relationship. At the high temperature range, the contribution of convection and liquid-phonon interaction increase significantly due to the fluidization of Li ions. Furthermore, there is an interplay between the enhanced phonon scattering and the increased forced hopping between neighboring atoms as temperature arises, which results in a dip in the evolution of the virial term around 1200K. When the temperature is higher than 1200 K, the virial thermal conductivity increases with temperature due to the contribution of vibrations with extremely short
mean free path (diffusons). At 1300 K, more than 46% of the heat carried by the S sublattice is contributed by the carriers with mean free path smaller than a few angstroms, which is the typical hopping distance. Our study provides a clear physical map of the heat transport in superionic battery materials and describes the key mechanisms to guide the design of thermal management in battery electrodes.

ES04.05.11
Investigation of LiPON Thin Films Grown by Pulsed Laser Deposition for Application as a Solid-State Electrolyte Thomas C. Callaway, David Beckwitt, Nick Rogers and Saibal Mitra; Physics, Astronomy, and Materials Science, Missouri State University, Springfield, Missouri, United States.

Modern lithium batteries use liquid electrolytes as the source for lithium ions in batteries and electrochromic devices. However, liquid electrolytes present its own set unique problems. Lithium ion batteries are prone to runaway thermal reactions and a loss of performance due to dendritic growth in the electrodes. Lithium phosphorous oxy-nitride (LiPON) is a solid-state material with good lithium ion conductivity that should address some of these challenges. In this work, we investigate the growth of LiPON films using pulsed-laser deposition (PLD) on pristine and copper-coated soda-lime glass. The goal of this work is to optimize the growth parameters for the development of highly conductive LiPON films that can be used in both solid-state lithium ion batteries and electrochromic devices. A lithium phosphate (Li3PO4) target was abladed in a nitrogen atmosphere using a Quantel Q-Smart 850 laser with a neodymium-doped yttrium aluminum garnet (Nd: YAG) crystal and a laser fluence of 20 J/cm². Two sets of films were deposited at room temperature and at 400°C. For each set of films the nitrogen pressure was varied from 10⁴ to 10⁶ mbar to 10⁻⁴ mbar. The target to substrate distance was held constant at 5.5 cm and the thickness of the films was controlled by the number of shots on the target. The films were studied both as-deposited and with a post deposition anneal of 30 minutes. We characterized the films using a number of techniques including x-ray diffraction, electron microscopy, Raman spectroscopy and electrical measurements. The detailed results will be presented.

ES04.05.12
Flexible Lithium-Air Batteries Based on Polymer Gel Electrolytes Lie Wang, Ye Zhang and Huisheng Peng; Fudan University, Shanghai, China.

The development of high-performance and flexible energy storage devices is critical while it remains challenging for wearable electronics. The lithium-air battery has been proposed as the next-generation energy-storage device with a much higher energy density compared with the conventional lithium-ion battery. However, they are designed into a rigid bulk structure that cannot meet the flexible requirement in the modern electronics. Besides, lithium-air batteries currently suffer enormous problems including parasitic reactions, low recyclability in air, degradation, and leakage of liquid electrolyte. Herein, a new family of all-solid-state lithium-air batteries was developed with high electrochemical performances and flexibility by designing a polymer gel electrolyte and an aligned carbon nanotube sheet air electrode. The battery exhibited a high discharge capacity and could stably work with long cycles in ambient air; its electrochemical performances were well maintained under bending and after bending, which is particularly desirable for portable and wearable electronic devices.

ES04.05.13
Combinatorial Study on Lithium-Ion Conductivity of Amorphous Li-La-Zr-O Thin-Films with Sol-Gel Processing Myung-Gil Kim; Chung-Ang University, Seoul, Korea (the Republic of).

The sol-gel process was successfully implemented for combinatorial investigation of amorphous Li-La-Zr-O (a-LLZO) electrolyte. With unlimited compositions of the amorphous structure, the combinatorial approaches were systematically developed to seek for optimal composition and optimized experimental condition (400 °C annealing temperature). The amorphous structures were displayed by GIXRD analysis. The electrochemical impedance study reveals that the ionic conductivity considerably improved with composition optimization, specifically from 4.8 x 10⁻⁸ S cm⁻¹ to 1.18 x 10⁻⁷ S cm⁻¹. Exceptionally, the LLZO-coated LiCoO2 (LCO) coin cell showed a greater cycling performance compared to bare-LCO coin cell at the optimum ratio of LLZO. We believe that a-LLZO is a promising material for solid electrolyte battery.

ES04.05.14
Highly Dense Composite Nanostructured Electrode for Flexible Supercapacitor Application Sangram K. Pradhan, Julien C. Niyogishima, Sangeeta Rout, Christian Carvajal, Bo Xiao and Messaoud Bahoura; Norfolk State University, Norfolk, Virginia, United States.

A high demand of energy storage devices has boosted researchers for fabricating ultra-efficient capacitor with better energy density and cycling stability. Supercapacitor made up of organic and inorganic nanostructured electrode showing better performance in terms of flexibility, light weight, and electrochemical stability. The supercapacitor made up of composite nanostructured electrode operates at higher voltage and exhibits excellent retention behavior with a very little loss of capacity even after few thousands of charge and discharge cycles. The composite electrode shows excellent flexibility without changing any sheet resistance even after few tens of bending mode. FESEM images reveals the formation of high dense nanostructure of different size with diameter vary from few tens to few hundreds of nanometer. The asymmetric supercapacitor shows energy density, power density of 0.47 mW h/g, and 35.2 mW h/g respectively. This device exhibits a high areal Csp of more than 6F/g. These energy storage unit holds a great potential for the use in future flexible electronic device.

ES04.05.15
Glucose-Intercalated NiMn LDH@NiCoS2 Heterostructures Supported on Carbon Fiber Cloth for High Performance Flexible Supercapacitors Shixia Chen¹ ² and Shuguang Deng¹; ¹School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; ²School of Resource, Environmental and Chemical Engineering, Nanchang University, Nanchang, China.

Weearable energy sources are under urgent demand due to the rapid development of wearable electronics. Supercapacitors possess a high power density and long cycle lifetime, thus developing flexible high-performance supercapacitors is a promising route to meet the demand for wearable energy sources. The realization of high-performance flexible supercapacitors strongly relies on the electrical properties and mechanical integrity of the constitutive materials and their ingenious assembly into free-standing and binderless structure. Pseudocapacitive metal (e.g., nickel, cobalt, and manganese) hydroxides/oxides provide multiple oxidation states for reversible Faradaic reactions which have been extensively pursued to realize efficient supercapacitors devices. However, the faradaic nature of bulk pseudocapacitive material with limited diffusion length restrains the capacitance contribution within the surface and near the surface of the material. Thus, a method to control the structure of the material should be found to improve the charge and ion-transfer efficiency of the flexible pseudocapacitive material. Core–shell structure with different pseudocapacitive materials can provide more electroactive sites, higher electrical conductivity, faster ion-electron transport, which might lead to unprecedented electrochemical performance. Herein, we design and fabricate a new and hierarchically core-shell structured hybrid of electroactive material coating (NiMn-glucose-LDH) on in situ grown NiCoS2 nanotube arrays on a flexible carbon fiber cloth (CFC), denoted as NiMn-G-LDH@NiCoS2. Highly conductive NiCoS2 nanotube arrays grown on a flexible CFC, which can serve not only as a superior pseudocapacitive material but also as a three-dimensional (3D) conductive scaffold for loading additional electroactive materials. Glucose intercalated NiMn LDH (NiMn-G-LDH) could significantly improve the ion diffusion coefficient with the expansion of the interlayer distance. Inheriting the merits of NiMn-G-LDH and NiCoS2 nanotube, the free-standing NiMn-G-LDH@NiCoS2 hybrid could synchronously achieve the excellent rate performance and cycle stability. The electrochemical investigation shows that the NiMn-G-LDH@NiCoS2 have a significantly enhanced specific capacitance (1,793 F g⁻¹ at 1 A g⁻¹), rate capability (~70% retention at 20 A g⁻¹) and cycling performance (keep ~82% after 1000 cycles) that far exceed those of the reported individual NiCoS2 and NiMn LDH electrodes.

ES04.05.16
Polymer-Mineral Composite Solid Electrolytes Bo Wang; Imerys, San Jose, California, United States.

Polymer-mineral composite solid electrolytes have been prepared using lithium ion-exchanged natural bentonite and mineral derived NASICON materials as solid electrolyte fillers in the polyethylene oxide (PEO) polymer containing LiTFSI salt. The mineral based solid electrolyte fillers not only increase ionic conductivity but also improve thermal and mechanical stability. The flexible and stretchy polymer-mineral composite solid electrolyte films can be used in the all-solid-state batteries.

ES04.05.17
1D Nickel-Cobalt Composite Oxides and Polypyrrole Decorated Stainless Steel Yarns for High-Performance Fiber-Shaped Flexible and Wearable Asymmetric

School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; 2School of Resource, Environmental and Chemical Engineering, Nanchang University, Nanchang, China.
Flexible and wearable supercapacitor (SC) has drawn a great attention for the potential in powering smart and wearable electronics. Particularly, 1D fiber-shaped flexible devices can be directly knitted or sewn into conventional textiles. Here, an electrodeposition strategy is devised to purposefully fabricate nickel/cobalt composite oxides and polypyrrole (PPy) decorated stainless steel yarns (SSY) as the positive and negative electrodes, respectively. The nickel/cobalt composite oxides based SSY positive electrode showed the highest volumetric capacitance of about 166.5 F/cm³ at the current density of 0.4 A/cm². Asymmetric all-solid-state supercapacitors (AASs) were then successfully developed and assembled by wrapping a PPy coated negative electrode on the as-prepared positive electrode in conjunction with the PVA/KOH gel electrolyte, showing competitive flexibility and electrochemical properties owing to the flexible SSY substrate and the highly pseudocapacitive materials. The as-obtained AASs exhibited a wide voltage window of 0-1.5 V, and the highest volumetric capacitance was nearly 13.88 F/cm³ at the current density of 20 mA/cm², and the maximum energy density was 2.95 mWh/cm³ at a power density of 17.68 mW/cm². Furthermore, the highly flexible AASs were then directly sewn into a conventional textile fabric, exhibiting great electrochemical stability under 6,000 charging/discharging cycles. Collectively, the work uses the highly pseudocapacitive materials and facile methods fabricated flexible AASs with enhanced electrochemical properties, which showed a decent potential in designing and exploring the next-generation wearable and portable SC devices.

SESSION ES04.06: Alkali Metal/Solid-Electrolyte Interface
Session Chairs: Jennifer Rupp and Jeff Sakamoto
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 122 A

8:30 AM *ES04.06.01
Interfacial Engineering of Solid-Solid Interfaces to Enable All Solid State Batteries Y. Shirley Meng; University of California, San Diego, La Jolla, California, United States.

Solidifying the components of a Li-ion battery consisting of a high energy capacity oxide cathode (e.g. NMC, NCA), a Li metal anode, and a sulfide-based glass ceramic solid electrolyte (SE), is a pathway to overcome the challenges of liquid electrolyte, namely dendrite growth and safety concerns without compromising high energy density. Even though the conductivity of a few sulfide solid electrolytes (SSEs) surpasses that of liquid electrolytes, multiple interfacial phenomena at both the cathode and anode interfaces play a crucial role in affecting efficient battery performance. Such phenomena include solid-electrolyte interphase (SEI) formation and mechanical deformation; the SEI forms due to poor chemical and electrochemical stability of SSEs while mechanical deformation arises from volume changes experienced by the cathode during cycling and also the rigid nature of SSEs. In the past several decades, tremendous effort has been made to study the SEI for SSEs, however, the properties of cathodic and anodic SEIs and their effects on long-term All Solid State Battery (ASSB) cycling are still not well-understood. In this work, we use multi-modal characterization and computation modeling tools to understand and elucidate the reaction mechanisms at the solid-solid interfaces. Interfacial engineering through coating of active electrode materials can be an effective method to enable ASSB at room temperature.

9:00 AM *ES04.06.02
Growth and Properties of Lithium Thin Films for Solid State Batteries Nancy Dudley1, Andrew S. Westover1, Erik G. Herbert2 and Jeff Sakamoto3; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Material science and engineering, Michigan Technological University, Houghton, Michigan, United States; 3University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

The lithium for many batteries comes packed in the cathode, so little is needed to seed the lithium anode and form the current collector. For this we grow the lithium films by vacuum thermal evaporation. This presentation will describe conditions and control of the film growth and the resulting morphology and properties of the films deposited onto a variety of solid electrolytes. Initial studies will also address how the lithium properties, structure and its interfaces evolve as functions of the rate and depth of the cycling.

Acknowledgement: The research was supported by the Advanced Battery Materials Research and Battery500 Consortium programs of Vehicles Technology Office within the US DOE’s Office of Energy Efficiency and Renewable Energy; and by the IONICS program of the Advanced Research Program Agency for Energy (ARPA-E).

9:30 AM ES04.06.03
Evaluating Changes at the Li-Metal/Solid-Electrolyte Interface Under Dynamic Stack Pressure Conditions Michael Wang and Jeff Sakamoto; University of Michigan, Ann Arbor, Michigan, United States.

Solid state electrolytes have the potential to enable safe, high energy-density Li metal batteries by serving as a physical barrier against unstable Li plating. Because of the tendency for Li filaments to propagate through the solid electrolyte and short circuit the cell at high current densities, significant emphasis has been placed on studying the kinetics and mechanisms of the plated Li-electrolyte interface. However, as the mechanics of the Li-metal/solid-electrolyte interface are drastically different from conventional Li-ion batteries, there is a continued need to understand the behavior of both Li metal stripping and plating. The present work evaluates the electrochemical behavior at the interfaces under dynamic stack pressure conditions. Using a novel mechanical testing apparatus in an inert environment, symmetric Li-electrolyte cells are studied under dynamic loading and electrochemical cycling conditions. Li₂La₂Zr₂O₇ (LLZO) garnet electrolytes are used as a model system, given the ability to achieve low interface resistances (~10Ω cm²) and stably plate Li at relatively high current densities. Using a combination of AC and DC methods, it is demonstrated that deviation from Ohmic behavior during constant current cycling occurs at a “critical stack-pressure” and is a result of surface roughening primarily at the Li stripping electrode. Changes in the interfacial resistance on the Li stripping electrode suggest the presence of Kirkendall voids which form when there is insufficient stack pressure to replenish the supply of Li being dissolved at the interface. The results further motivate the need to understand the coupled electrochemo-mechanical behavior of the Li-metal/solid-electrolyte interface and identifies stack pressure as an important design parameter for future solid-state batteries.

9:45 AM ES04.06.04
Garnet Based Solid Electrolyte Lithium-Ion Battery for Safe Energy Storage Application Samuel Dantuah, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, Chesapeake, Virginia, United States.

Fast-ion-conducting garnet-type solid electrolyte could influence solid-state battery chemistries with desirable performance and safety. In addition, it is environmentally stable and has an electrochemical window wide enough to overpower surplus electronic transport. However, high interfacial resistance at the electrode/solid electrolyte interface makes it more challenging for commercial use, which consequently, hinders the fast charging and discharging behavior of the battery. This work investigates the reduction of the high interfacial resistance at the electrodes/solid electrolyte interface using a garnet material Li₆La₂Zr₂(CO₃)₂Zr₂Ti₅Nb₂O₁₉ (LLCNN) synthesized by a wet chemical technique and ultrathin hafnium oxide (HfO₂) by atomic layer deposition technique. A remarkable reduction of the interfacial impedance was noticed at room temperature. The structure and surface morphology of LLCNN and HfO₂ were characterized by X-ray diffraction (XRD) and FESEM respectively. Interestingly, field emission scanning electron microscope (FESEM) images show the porosity of the electrolyte which helps for the easy movement of charged ions through the electrolyte. The electrochemical performance of the battery shows outstanding performance with large charge storage capability. The battery shows improved capacitance with higher number of charging and discharging cycles. This improvement in the rate ability is a result of the reduction in the interfacial impedance. This work is supported by the NSF-CREST (CREAM) Grant Number HRD 1547771, and NSF-CREST (CNBMD) Grant number HRD 1036494.

10:00 AM BREAK

10:30 AM ES04.06.05
Unexpected Opportunities in Stabilizing Lithium Metal Anodes Using Soft Solid-Ion Conductors Brett Helme1, Chengyin Fu1, Andrew Ellis1, Zeeshan Ahmad2, Victor Venturi2 and Venkat Viswanathan1; 1Lawrence Berkeley National Lab, Berkeley, California, United States; 2Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.
The realization of a low-cost, safe, reversible, high-area capacity lithium metal electrode for solid-state batteries has remained elusive despite ongoing advances in anode protection using ion-conducting ceramics and glasses as well as organic and inorganic passivating layers. Here, we will outline a framework to understand the successes and failures of these differentiated materials platforms on the basis of their mechanical properties, transport properties, and partial molar volume considerations for solid-ion conductors relative to the lithium anode. Within this framework, I will also highlight an unexpected opportunity for suppressing lithium metal dendrites using soft solid-ion conductors. I will then detail the extent to which these predictions deliver on their promise, from early-stage discovery science and in-depth synchrotron hard x-ray techniques to platform maturation from coin cells to pouch cells.

10:45 AM ES04.06.06
Dendritic Growth in Lithium-Based Batteries Aarun Jair
Sang Im Woo, Karra S. Vikrant and Edwin Garcia; Purdue Univ, West Lafayette, Indiana, United States.

Lithium dendrite growth is one of the grand challenges in the design of high energy rechargeable lithium-ion batteries. “Dendrites” are undesired elongated metallic nanostructures that form on the anode during fast charging. Upon battery cycling, they grow towards the cathode causing short-circuits and other catastrophic failures (including fires) in portable electronic devices and electric vehicles. A computational framework based on the Phase Field Method has been developed to couple lithium electrodeposition kinetics on the anode with the inherent mechanical behavior of metallic lithium. The framework provides a means to provide detailed insight on the time-dependent, spatially heterogeneous electrical, chemical, and mechanical driving forces during electrodeposition that are otherwise difficult to visualize through experiments. The different mechanisms observed during classical electrodeposition and those previously unidentified are predicted and rationalized through this framework as a stepping stone to design safer, high energy density devices.

11:00 AM ES04.06.07
Mechanisms of Critical Current Densities in Solid Electrolytes for Preventing the Lithium Metal Penetration Peng Bai and Jizhao Guo; Washington University in St. Louis, St. Louis, Missouri, United States.

Li-ion batteries are currently the most energy-dense battery technology. If the intercalation anode (e.g. graphite) can be completely removed and Li ions stored in the intercalation cathode can be reduced into a thin film of Li metal anode during recharge, the energy density of the state-of-the-art Li-ion battery will be nearly doubled. However, the formation of Li metal anode in liquid electrolytes has been plagued by the dendrite penetration and low cycling efficiency for decades [1,2]. While solid electrolytes in principle could solve both problems, recent studies revealed that Li metal dendrites can easily penetrate the garnet Li$_2$Zr$_2$O$_7$ (LLZO) solid electrolyte at current densities lower than 1 mA cm$^{-2}$ [3-12]. This relatively low critical current density (CCD) prohibits the battery using solid electrolyte from fast charging, therefore will significantly limit the application, especially for electric vehicles. Accurately understanding the mechanisms of CCD has become an urgent need for designing high-rate, dendrite-proof solid electrolytes. In this study, we first analyzed 16 sets of reported experimental data, and discovered for the first time a linear relationship between the CCD, $J_{lim}$, and the thickness of the solid electrolyte pellet, $L$, i.e. $J_{lim} \propto \sigma_{metal}/L$. This linear relationship resembles the proved limiting current in liquid electrolytes, i.e. $J_{lim} \propto D_{L,L,L}/L$ [1], suggesting that the solid electrolyte may also have a limiting current, even though prevailing understandings prefer that the near unity transference number ensures an infinitely high limiting current. Inspired by the electrochemical methods used in studying lithium electrodeposition in liquid electrolytes, further investigations of the transport properties of LLZO solid electrolytes led to the discovery of the limiting current in the $L$-$V$ curve, which is consistent with the CCD discovered from the standard constant current cycling. Quantitative explanations and a simple mathematical model were provided to better understand the mechanisms of the CCD.

References

11:15 AM ES04.06.08
Mechanical Properties of Metallic Sodium and Metallic Lithium Anodes Coleman D. Fincher, George M. Pharr and Matt Pharr; Texas A&M University, College Station, Texas, United States.

Room temperature metallic anodes possess potential to enable batteries with enormous capacity. Lithium metal is known as the “holy grail” of anode materials, as it has the highest theoretical capacity, lowest density, and most negative electrochemical potential of known anode materials for rechargeable batteries. However, dendrites of lithium form during repeated cycling, posing a significant safety hazard. Sodium has similar safety concerns and a much larger sized ion than lithium (1.02 Å versus 0.59 Å), leading to generally comparatively worse kinetic performance. Despite their issues, sodium metal anodes have recently received increased attention due to sodium’s natural abundance and relatively low cost. A comprehensive understanding of both lithium’s and sodium’s mechanical properties is vital in designing solid-state electrolytes to mitigate dendritic growth. Through nanoindentation and bulk tensile testing, we explore the mechanical properties of the metallic sodium and lithium anode.

11:30 AM ES04.06.09
Mechanistic Origins of Lithium Plating with Solid Electrolytes Aashutosh Mistry and Partha P. Mukherjee; Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States.

Solid electrolytes are advocates for next-generation lithium batteries given their conformity against lithium metal anodes. Intuitively the mechanical stiffness of the solid electrolytes should discourage irregular lithium deposition. However, often lithium dendrites are found to form in solid electrolytes. We find that the solid electrolytes defy the conventional wisdom of electroplating. An irregular lithium dendrite leads to a misfit strain which alters both the reaction kinetics and transport in the solid electrolyte. These competing mechanisms give rise to an interfacial instability, which marks the onset of dendrite formation. Here in we discuss the regimes to promote uniform deposition.

SESSION ES04.07: Solid-Solid Interfaces
Session Chairs: Juan Carlos Gonzalez-Rosillo and Juergen Janek
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 122 A

1:30 PM *ES04.07.01
Enabling All-Solid Lithium-Sulfur Batteries Timothy Arthur; Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

To meet the future demands of future hybrid, plug-in hybrid, and all electric vehicles, advances in energy storage for transportation is indispensable. Additionally, energy diversification is vital to tailor electrification requirements to optimize the cost, range and size of the application. Recently, post Li-ion batteries, such as Li-O$_2$, multivalent and anion batteries, have garnered much attention. The lithium-metal/sulfur (Li-S) battery is an exciting system due to its high theoretical capacity (1673 mAh/g) and the potential of low cost. However, realizing Li-S batteries relies on solving key challenges such as dissolution and shuttling of polysulfides, low sulfur utilization at high-areal loading levels,
lithium metal dendrite formation, and continuous electrolyte decomposition on the Li metal surface. The potential benefits of solid-state electrolytes, such as polymer electrolytes, gel electrolytes and ion-conducting ceramics electrolytes, are wide-operating windows, active material dissolution prevention and metal dendrite inhibition. However, low ionic conductivity and interfacial stability require continued development to achieve a viable energy storage system. Recently, ionic conductivities rivaling liquid based-systems have been observed for the sulfide-based, glass-ceramic Li2O/GeS2/LGPS, encouraging continued research into solid-state batteries using sulfide-based solid-electrolytes. Tatsumisago et al. illustrated and impressively initial cycling results using lithium-iodium alloy anode, a lithium iodide/lithium sulfide solid-solution cathode, and a solid sulfide electrolyte: over 1000 mAh/g at 2C cycling for over 2000 cycles. Inspired by the results, developing all solid Li-S (AS-LiS) batteries presents hope for a high-energy density battery.

The major road-block to enabling AS-LiS batteries lies is the capability to utilize lithium metal. Researchers have recently observed the decomposition of sulfide electrolytes in contact with lithium metal, as well as the tendency for the active metal to plate within the electrolyte layer and create electrical shorts. The realization of lithium metal for solid-state batteries will provide the energy needed for future mobility. Here, we will discuss protection strategies to inhibit undesired reactions at the anode-electrolyte interface; including lithium metal surface modification, and additives for the solid-electrolyte separator layer as potential solutions. Realizing lithium metal for solid-state batteries will provide the energy needed for future mobility.

Solid-state batteries (SSBs) have been regarded as promising next-generation Li-ion batteries (LIBs), and promising solid electrolytes (SEs) with higher Li-ion conductivities have been found. However, the high interfacial resistance of Li-ion transport at the electrode-SE interface remains a crucial bottleneck. Although interposing a buffer layer into the interface has been used to remedy this problem in practice [1], the fundamental mechanism is still under considerable debate. We have been exploring the atomistic understanding of this interfacial resistance mechanism with DFT-based calculation approaches [2-3]. So far we have devised some systematic ways for the solid-solid interfaces and discussed possible origins such as the space-charge layer and the reaction layer. However, the sufficient sampling of the solid-solid interface configurations is too cumbersome for deducing any significant statistical and general features of the interfacial Li-ion transport. Hence, we utilized the CALYPSO structure prediction method [4,5] as a calculation technique for the interface structure search, to be combined with mismatch treatment, lateral shift etc.

Here as representative model systems, we applied the above DFT-based calculation technique Li/LCO (LCO = LiCoO2), Li/LPS (LPS = Li3PS4), and Li/NbO2 (LNO) acting as a cathode, a sulfide electrolyte, and a buffer layer, respectively. For the LCO/LPS interfaces, we sampled over 20000 configurations and found several stable disordered structures involving ionization and anion exchange, leading to the formation of a reaction layer. On the other hand, Li-ion sites that can be preferentially depleted upon charging always exist around the cathode-SE interfaces irrespective of the interfacial order/disorder. Therefore, we conclude that the dynamic Li-ion depletion is likely to be a major cause that prevents successive Li-ion transport, leading to the resistance. Through investigating the buffer layer effects and the interfacial electronic states, we also deduced a probable origin for the interfacial Li depletion and a mean to suppress this problematic behavior. In the talk, we will also discuss the related works on anodes and SEI interfaces.

References:

Modeling the Origin of the Interface Resistance in Solid-State Batteries Yue Qi, Michael Swift and Hong Kang Tian; Michigan State University, East Lansing, Michigan, United States.

The major bottleneck for the all-solid-state batteries lies at the high interfacial resistance, which is due to two main factors, physical contact and chemical effect, both will be evaluated via modeling in this talk. First, we devise a model, incorporating atomic electrochemical potentials, thermodynamic stability of bulk electrolyte phases, and point defect formation energies to yield quantitative profiles of the electrostatic potential, lithium chemical potential, and electronic energy levels. This model complements direct microscopic and macroscopic simulations by rigorously and simultaneously determining the potential drop, electrostatic dipole, and space-charge layer at the interface. The application of this model to the Li/LiPON/LixCoO2 system leads to the important discovery that the space-charge layer varies with the state of charge (i.e. Li concentration in LixCoO2). This new physics insight unifies the seemingly contradictory experimental observations and leads to new device design rules to promote interfacial ion transport in future solid-state-batteries. Secondly, we combined contact mechanics with 1D Newman battery model to capture the effect of imperfect electrode/electrolyte interfacial contacts, which can be formed during cell fabrication and worsened due to cycling of solid-state-batteries. Constant current discharging processes at different rates and contact areas were simulated to correlate the capacity drop with the contact area loss. Furthermore, the model suggested how much pressures should be applied to recover the capacity drop due to contact area loss.

Low Temperature Processing Innovation and Structure Design of Li-Garnets for Solid State Batteries and Environmental Sensing of Chemicals Juan Carlos Gonzalez-Rosillo and Jennifer L. Rupp; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Next generation of energy storage and sensors may largely benefit from fast Li+ ceramic electrolyte conductors to allow for safe and efficient batteries and real-time monitoring anthropogenic CO2. Recently, Li-solid state conductors based on Li-garnet structures received attention due to their fast transfer properties and safe operation over a wide temperature range. Through this presentation basic theory and history of Li-garnets will first be introduced and critically reflected towards new device opportunities demonstrating that these electrolytes may be the start of an era to not only store energy or sense the environment but also to emulate environmental data and information based on simple electrochemistry device architecture twists. In the first part we focus on the fundamental investigation of the electro-chemo-mechanical characteristics and design of disordered to crystallizing Li-garnet structure types and their description. Understanding the fundamental transport in solid state and asking the provocative question: how do Li- amorphous to crystalline structures conduct? New insights on degree of glassy to crystalline Li-garnet thin films are presented based on model experiments of the structure types. Here, the thermodynamic stability range of maximum Li-conduction, phase, nucleation and growth of nanostructure is discussed using high resolution TEM studies, near order Raman investigations on the Li-bands and electrochemical transport measurements. In a second part, we focus on new processing opportunities to Li-garnet thin films in crystalline state and to assure cubic and fast conducting garnet structures for thin film form. For this we will review the field of thin film processing and structure-property for garnet type thin films and reflect our recent new processing routes based on vacuum and wet-chemical techniques. The insights provide novel aspects of glass and ceramic thin film processing and material structure designs for both the Li-garnet structures (bulk to films) and their interfaces to electrodes, which we either functionalize to store energy for next generation solid state batteries or ... make new applications such as Li-operated CO2 sensor tracker chips which we present in a final part.

An Analysis of Kinetics at the Solid Polymer Electrolyte/Lithium Lanthanum Zirconium Oxide Electrolyte Interface Arushi Gupta and Jeff Sakamoto; University of...
Polymer-Lithium Lanthanum Zirconium oxide (LLZO) composites have gained traction as a promising candidate to be used as electrolytes for solid state batteries. They can exhibit high ionic conductivity and suitable mechanical properties owing to the complementary characteristics of the ceramic and polymer respectively. However, without intervention, the polymer-ceramic interface is highly resistive. Thus, to achieve facile ion transport across the polymer-ceramic interface it is necessary to minimize the interfacial resistance. We hypothesize that two important factors which limit the interfacial kinetics between the two electrolyte faces: 1) surface impurities on the LLZO electrolyte and 2) a large disparity in charge carrier concentration the polymer electrolyte (Polyethylene oxide (PEO)-LiTFSI) and LLZO.

Firstly, we studied the effect of the LLZO heat treatment (HT) temperature on the interfacial impedance between LLZO and PEO-LiTFSI (27:1 [EO]/[Li]+ ratio) using a trimilaniar PEO-LiTFSI/LLZO/PEO-LiTFSI cell configuration. We determined that the interfacial impedance decreased exponentially with increasing LLZO HT temperature. Secondly, we believe that by increasing the Li concentration we would facilitate charge transfer at PEO-LiTFSI/LLZO interface. For this we studied the effect of Li salt concentration in the polymer electrolyte on the interfacial impedance, observing that the interfacial impedance decreases with increasing salt concentration. We achieved an interfacial impedance value of ~390 Ohms cm² at the optimal [EO]/[Li]+ salt concentration.

With the results from the two studies, we believe we can further lower the interfacial impedances, achieve facile Li ion transport across the PEO-LiTFSI/LLZO interface and thereby, enable the development of composite electrolytes with high room temperature ionic conductivities.

4:00 PM ES04.07.06
Degradation Mechanisms in All-Solid-State Li-S Batteries with LiPSCl and Their Optimization Sanevuki Ohno, Georg Dewald, Juergen Janek and Wolfgang Zeier; Justus Liebig University Giessen, Giessen, Germany.

While the demand for batteries with a high energy density is rapidly growing, the currently commercially available Li-ion battery chemistry is approaching a theoretical limit. To overcome this issue, Li-S batteries exploiting the conversion reaction between sulfur and Li+S have been attracting significant attention as a promising candidate for next-generation batteries. The history of the development of conventional Li-S batteries has involved the fight against the notorious shuttle effect caused by polysulfides dissolved in the liquid electrolyte. However, employing solid electrolytes as a separator can mitigate the occurrence of this polysulfide shuttle. Indeed, solid-state Li-S batteries composed of Li-ion conducting thio-sphosphates (e.g. Li5PS4Cl), exhibit no evidence of the shuttle effect.

Nevertheless, there are still several major challenges hindering the development of batteries exhibiting a high capacity and good capacity retention. In this study, the mechanisms of short-term and long-term capacity fade within solid-state Li-S batteries employing LiPS2Cl are investigated. The cause of a crucial capacity loss observed after the initial discharge is elucidated and overcome using a facile cathode processing method, thereby resulting in a specific capacity of over 1000 mAhg−1. The degradation process affecting the battery performance during long-term cycling are also investigated. Using the results from our investigations toward the optimization of the aforementioned battery architecture, we were able to achieve a specific capacity of 700 mAhg−1 after 100 cycles. A deeper understanding of the underlying chemistry influencing crucial degradation mechanisms will enable further enhancements of both the capacity and cyclability of solid-state Li-S batteries.

References:

4:15 PM ES04.07.07
Interface Stability Between Solid-State Electrolytes and Cathodes in Lithium-Ion Batteries Jung-Hyun Kim1, Chan-Yeop Yu1, Jun-Bin Choi2 and Venkataramani Anandar1; 1Mechanical and Aerospace Engineering, Center for Automotive Research, The Ohio State University, Columbus, Ohio, United States; 2Energy Storage Research Department, Ford Motor Company, Dearborn, Michigan, United States.

Although lithium-ion (Li-ion) battery is one of the most successful energy storage devices, especially for electric vehicle (EV) applications, it retains a thermal runaway risk that stems from the presence of flammable liquid electrolytes made of organic solvents. To overcome this challenge, significant research efforts have been recently devoted on the development of new ceramic electrolytes that can replace the flammable liquid electrolyte and yield an all-solid-state Li-ion batteries. Among various solid electrolytes investigated, Li1.25Al0.75La2Zr1/3Ta1/3O2 (LLZT) with garnet structure and Li1.25Al0.75Ti1/3P0.5 (2P0.5) (LATP) in NASICON family showed great promises due to their stabilities in air, high-voltage stability, good mechanical properties, and reasonable Li-ion conductivity (10−2 − 10−3 S/cm).

Despite the significant progress in discovering new ceramic electrolytes with promising Li-ion conductivity, a ceramic-based solid-state battery is not commercially available today. The main barrier for a scale-up of solid-state batteries as practical power sources is the instability of electrode-ceramic electrolyte interface and the consequent premature cell-failure. In particular, the fabrication processes of solid-state batteries involve high-temperature heat-treatment to obtain good adhesions between ceramic components. During the sintering process, unwanted elemental inter-diffusion between the electrodes and electrolytes can occur and form secondary phases at interfaces, which often impede the transportation of Li-ions at the interfaces.

In this presentation, we will report our recent systematic study on the interface stability between solid-state electrolytes (e.g., LLZT or LATP) and conventional cathodes in Li-ion batteries including various chemical compositions and crystal structures (e.g., LiCoO2, LiNiO2, LiNi0.05Co0.95Mn0.03O2, LiNi0.5Mn0.15O2, and LiFePO4). First, we investigated high-temperature phase stabilities between solid-electrolyte and cathode composites, characterized by X-ray diffractionometer (XRD) and Rietveld refinement in a temperature range of 500 – 900°C in air. By identifying crystalline phases at each temperature, we can find (1) on-set temperatures of unwanted side-reactions between solid-electrolytes and cathodes, (2) types of secondary phases and their evolutions depending on temperature, and (3) fundamental reaction mechanisms between different types of solid cathodes and electrolyte materials. In addition to the thermodynamic stabilities at interfaces, we will present the effect of interface stability and microstructure on the electrochemical performances at cathode/solid-electrolyte interfaces. From electrochemical impedance spectroscopy (EIS) and adhesion test combined with scanning electron microscopy (SEM), increasing a sintering temperature offers a trade-off between good adhesion of cathodes and interface stability, which significantly impacts the electrochemical performances of solid-state Li-ion batteries. Therefore, by exploring the phase stability – microstructure – electrochemical performances relationship, we can find the optimal sintering conditions of cathode/solid-electrolyte interfaces.

The results from our systematic study will be essential in determining processing parameters of solid-state Li-ion batteries. Moreover, understanding the fundamental reaction mechanisms between solid-electrolytes and cathode materials will be a prerequisite for a design new solid electrolyte – cathode interfaces in future studies.

4:30 PM ES04.07.08
Enhanced Grain Growth Kinetics in Polycrystalline Li5.25Al0.75La2Zr1/3Ta1/3O2 Solid Electrolyte Regina Garcia-Mendez and Jeff Sakamoto; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

The demand for vehicle electrification has created the impetus to develop energy storage technology beyond Li-ion. One approach involves the use solid electrolytes to enable metallic Li anodes, pushing energy densities to 1200 Wh/L. However, the ability to plate Li metal at relatively high current densities (~3 mA/cm²), has not been demonstrated using solid electrolytes. Moreover, it was reported [1] that in polycrystalline solid electrolyte such as Li5.25Al0.75La2Zr1/3Ta1/3O2 (LLZO), Li preferentially deposits intergranularly. We hypothesize that the maximum Li plating rate (or critical current density – CCD) is strongly correlated to the existence of microstructural defects, such as grain boundaries, as
interest in solid-state electrolytes has grown rapidly in recent years owing to the desire to utilize Li metal anode for improved specific energy density and the inherent safety advantage of a non-flammable solid state electrolyte. A practical solid electrolyte for energy storage must be a fast ion conductor, have negligible electronic conductivity, high relative density and adequate chemical and electrochemical stability with electrodes. For ease of manufacturing and potentially higher power capability we have focused research on oxide ceramic electrolytes. This work will cover our work on the synthesis and characterization of NASICON, perovskite, garnet and newly emergent structural families including how to stabilize the most conductive phase and maximize the ionic conductivity through substitutional chemistry. We will discuss materials synthesis, ionic/electronic conductivity, mechanical properties, Li/water stability and the results will be compared and contrasted for varied structural families of Li-ion solid electrolyte conductors.

**SESSION ES04.08: Solid-State Electrolyte Synthesis and Processing**

**8:00 AM ES04.08.01**

**Synthesis and Characterization of Fast Li-Ion Conducting Solid State-Electrolytes**

Jan L. Allen; U.S. Army Research Laboratory, Adelphia, Maryland, United States.

Interest in solid-state electrolytes has grown rapidly in recent years owing to the desire to utilize Li metal anode for improved specific energy density and the inherent safety advantage of a non-flammable solid state electrolyte. A practical solid electrolyte for energy storage must be a fast ion conductor, have negligible electronic conductivity, high relative density and adequate chemical and electrochemical stability with electrodes. For ease of manufacturing and potentially higher power capability we have focused research on oxide ceramic electrolytes. This work will cover our work on the synthesis and characterization of NASICON, perovskite, garnet and newly emergent structural families including how to stabilize the most conductive phase and maximize the ionic conductivity through substitutional chemistry. We will discuss materials synthesis, ionic/electronic conductivity, mechanical properties, Li/water stability and the results will be compared and contrasted for varied structural families of Li-ion solid electrolyte conductors.


**8:30 AM ES04.08.02**

**Adapting Materials Processing and Structure Toward Improved NaSICON-Based Sodium Ion Conductors**


Creating new, high conductivity, zero-crossover solid state separators is central to the advance of emerging solid state and other high energy density batteries. In particular, we are synthesizing sodium ion conductors could enable new classes of low cost, high performance systems. Here, we focus on recent progress advancing sodium ion conductors based on materials such as NaSICON or β'-alumina, which typically require elevated temperatures (~250-350°C) for optimal ionic conductivity. Lowering the usable temperature of these materials makes them much more practical for applications such as solid-state batteries. NaSICON ceramics, in particular, are recognized for potential as room temperature sodium ion conductors, and here we highlight our efforts to tailor the composition and structure of NaSICON-based solid state separators for use in ambient or near-ambient applications. We not only explore how variations in NaSICON chemistry can affect conductivity, but also how processing these materials into hybrid architectures and composite materials promises improvements in separator conductance and overall separator performance. We specifically discuss material design, processing, and characterization of separator properties, focusing not only on ionic conductivity, but also on challenges to mechanical behavior and chemical stability of these materials that affect battery safety and long term performance. These emerging solid state separators offer great promise toward a new class of robust and reliable energy storage technologies.


**8:45 AM ES04.08.03**

**On Thin-Film LLZO Electrolytes for All-Solid-State Batteries**

Jordi Sastre-Pellicer¹, Agnieszka Priebe², Ayodhya N. Tiwari³, Yaroslav E. Romanyuk⁴ and Stephan Buecheler¹; ¹Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; ²Laboratory for Mechanics of Materials and Nanostructure, Empa-Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland.

The concept of all-solid-state Li-ion batteries has gained broad attention in recent years as it has the potential to overcome the energy density and safety limitations of the nowadays widely used Li-ion batteries based on liquid electrolytes. Thin film manufacturing opens up the possibility of further enhancing volumetric and gravimetric energy densities by reducing the amount of inactive materials, lower the costs of production, and enable new applications, like on-chip batteries.

Garnet-type Li₁₀.₃La₂Zr₂O₁₂ (LLZO) electrolyte is a promising ionic conductor, for the development of all-solid-state thin-film batteries. While high ionic conductivities (above 1 mS/cm) have been demonstrated for bulk material in pellet form, processing LLZO in the form of thin films still poses some challenges. Ionic conductivities reported so far are generally much lower than those of the bulk material, densities and conformability are difficult to achieve at the limited sintering temperatures required.

In our work we investigated LLZO thin films deposited by co-sputtering from LLZO, Li₂O and Al₂O₃ targets, and subsequently annealed under a controlled oxidizing atmosphere. In this work, the LLZO thin films were sputtered onto 200 μm thick Si wafers at 100 °C, and annealed in a muffle furnace at 300 °C, 500 °C, and 700 °C. The thickness of the LLZO thin films was measured using a surface profilometer. The density of the LLZO thin films was determined using Archimedes’ method. The ionic conductivity of the LLZO thin films was measured using a four-point probe technique.

In our contribution we will present successful approaches to increase the ionic conductivity of LLZO thin films above 10⁻² S/cm and achieve higher density, uniformity and surface stability, which are key attributes necessary for the implementation of a LLZO-based thin-film battery with a metallic Li anode. In particular, we will discuss how we tackled common challenges in the fabrication of thin-film ceramic Li-ion electrolytes: the stabilization of highly conductive phases at room temperature, the compensation of Li losses during annealing, the densification of the films at relatively low temperatures, and the mitigation of moisture-induced surface degradation.

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route to obtain garnets with both particle size and high ionic conductivity. Acting as high temperature solvents, molten salts present a large design space wherein the properties of the salt melt can be finely tuned to present desirable properties in the as-synthesized material. Further, modifying the basicity of the salt melt enables simultaneous substantial reduction in the formation temperature of complex oxides, which is expected to drastically lower the energy cost of synthesis of lithium conducting garnets. However, the increased complexity of chemistry in molten salts presents a non-trivial challenge, requiring finer tuning of both the molten salt medium and precursors to take full advantage of the benefits offered by MSS to obtain pure material. In particular, relative solubility of reagents as well as the stability of LLZO in a given salt melt have substantial implications on crystal chemistry, phase purity, and performance. The work described herein explores a wide range of salt media including ‘neutral’ media (e.g. molten halides) and basic media (e.g. molten oxoalts), as well as the effect of certain additives, in the synthesis of lithium conducting garnets. Design principles for formation of doped and co-doped LLZO are discussed, wherein salt and reagent composition have direct effects on the formation temperature, particle size, particle size distribution, and electrochemical performance of the as-synthesized material. Depending on the choice of salt medium, powders consisting of single-crystals of LLZO with tunable particle size between 0.5 to 20 μm can be obtained at temperatures as low as 500 °C, while maintaining high ionic conductivity, demonstrating the versatility of the MSS approach for this crucial class of ionic conducting materials.

9:15 AM ES04.08.05 Computational Study of Lithiation of Ba-Doped Type I Si/Ge Clathrates Xiaohong Peng1, Andrew Doplilka1, Qun Wei1,2 and Candace K. Chan1; 1Arizona State University, Mesa, Arizona, United States; 2Physics and Optoelectronic, Xidian University, Xi'an, China.

Types I and II Si and Ge clathrate materials have recently been studied for their electrochemical properties as anodes for lithium-ion batteries due to their unique cage structures and ability to incorporate extrinsic guest atoms. First-principles density functional theory (DFT) calculations were performed to investigate the type I Si and Ge clathrate compounds with and without the guest Ba atoms to understand the optimal structural configurations of small degrees of lithiation and Li diffusion paths inside the clathrates. The studied structures include Si60, Li,Na16Si64, Li,Na16,As8,Na16 and Li,Na16Ge43. The results showed that Li insertion into framework or Ba vacancies could stabilize the clathrate structures. Substitution of Si network atoms by Al lowered the formation energies of the lithiated compounds and mitigated the calculated volume increase upon lithiation. The results also showed that it is energetically feasible for multiple guest atoms to be placed in the Si60 cages. For Ba-doped Ge clathrates, it was found that Li insertion into the three framework vacancies in BaGe43 is energetically favorable, with a calculated lithiation voltage of 0.77 V versus Li/Li+. However, the high energy barrier (1.6 eV) for Li diffusion between vacancies and around Ba guest atoms suggests that framework vacancies are unlikely to significantly contribute to lithiation processes unless the Ba guest atoms are absent. The results from this study can elucidate the preferred structural configurations for Li in type I, Ba-doped Si and Ge clathrates and also be informative for efforts related to understanding the structures obtained after electrochemical insertion of Li into the clathrates.

9:30 AM BREAK

10:00 AM ES04.08.06 Electron Microscopy for All-Solid-State Batteries—Addressing Challenges at Atomic Scale Miaofang Chi; Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

All solid-state batteries are considered as one of the primary battery configurations that offers cost-effective and efficient energy storage. Recently, several solid electrolyte materials have been developed that exhibit ionic conductivities that are equivalent to that of organic liquid electrolytes. Low ion conductivities that were previously believed to be the major issue impeding the use of solid electrolytes are no longer the bottleneck. Rather, their interfaces are frequently found to limit the performance of all solid-state batteries. These interfaces include both internal interfaces such as grain boundaries and the interfaces between two electrolytes if the solid electrolyte is a composite or a multilayered material. The associated challenges now include electronic conductivity, mechanical integrity, chemical, and electrochemical instabilities that result in limited current densities, inadequate cyclability, and dendrite growth. These phenomena, however, are challenging to characterize and understand since they are often spatially confined and embedded. Owing to its atomic-level spatial resolution for both imaging and spectroscopy, scanning transmission electron microscopy (STEM) is now a primary technique for addressing the challenges in such studies. This talk will focus on introducing how we use state-of-the-art atomic-resolution STEM and electron energy loss spectroscopy (EELS) to understand the complex phenomena at interfaces in all solid-state batteries. I will also introduce emerging STEM techniques, such as 4D-STEM based differential phase contrast (DPC) imaging and vibrational spectroscopy, and discuss how these methods can benefit research of solid-state ionic materials. I will touch on the importance of understanding synthesis mechanisms regarding interfaces by highlighting examples of our recent work aimed at elucidating synthesis and processing mechanisms of solid electrolytes using in situ electron microscopy and neutral scattering. This work was sponsored by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, the Materials Sciences and Engineering Division, and was performed at ORNL’s Center for Nanophase Materials Sciences (CNMS), which is an Office of Science User Facility.

10:30 AM ES04.08.07 Green Synthesis of Size-Controlled Li,S Nanocrystals for Use in Solid State Batteries Yangzhi Zhao, Kristen Hietala, Yongan Yang and Colin A. Wolden; Colorado School of Mines, Golden, Colorado, United States.

Lithium sulfide (Li,S) nanocrystals (NCs) are critical materials used to produce solid-state electrolytes and cathodes for emerging battery technologies. Li,S is typically produced by high temperature carbothermal reduction that creates powders, which then require extensive ball milling to produce the nano-sized materials desirable for battery applications. We have recently developed a solution-based synthesis of Li,S nanocrystals by contacting metalorganic solutions with hydrogen sulfide at ambient temperature, employing bubble columns for scalable production. Additional benefits include complete abatement of H2S and recovery of the valuable H2 stored within. Control of nanocrystal size and uniformity is demonstrated through choice of solvent and manipulation of processing conditions such as precursor concentration and solvent evaporation rate. X-ray diffraction (XRD), small angle X-ray scattering (SAXS), and scanning electron microscopy (SEM) were used to quantify crystallinity, particle size distribution (PSD), and morphology, respectively. These complementary techniques confirmed the production of anhydrous, phase-pure Li,S nanocrystals with tunable size (5-40 nm) and narrow PSDs. Mild annealing conditions were identified that provide the purity required for battery applications, while retaining the original PSD. These materials were used to synthesize simple cathodes and solid-state electrolytes to validate their electrochemical properties. Li,S cathodes fabricated using NCs (<10 nm) achieved capacities approaching the theoretical limit (1166 mAh/g), exhibiting good rate capability and promising stability. Control of size is also expected to provide many benefits for solid-state electrolyte production including reduced thermal budgets, improved ionic conductivity, and minimized interfacial resistance. Studies are underway to fabricate Li,S-P,S cathode electrolytes, where it has already been shown that the use of NCs dramatically shortens the ball mixing time required to create the glassy phase relative to commercial powders. We will report on the electrochemical performance of these electrolytes and the integration of these materials in solid-state architectures.

10:45 AM ES04.08.08 Unusual Temperature Dependent Li-ion Conductivity and Influence of Air Exposure on NASICON-type Solid Electrolyte Hirotoshi Yamada1, Taiki Nakamura1, Eiisuke Magome2 and Tomoko Ito1; 1Nagasaki University, Nagasaki, Japan; 2Saga Light Source, Tosu, Japan.

Some of lithium-ion conducting solid electrolytes with rather high ionic conductivity exhibit high sensitivity to air. It is well known that sulfide-based ones hydrolize. Even oxide-based ones, garnet-type lithium ion conductors react with air, resulting in formation of LiOH and Li2CO3 on their surface and deterioration of conductivity. Among them, NASICON-type solid electrolytes, such as LiAl1/2Ti1/2(PO4)3 (LATP), have been supposed to be stable in air. In this study, we have found that unusual temperature-dependent ionic conductivity of LATP: ionic conductivity showed negative activation energy from 0 to ~15°C on cooling. Detailed studies using high-frequency electrochemical impedance spectroscopy and synchrotron X-ray diffraction confirmed that the unusual temperature-dependence is due to the change in grain boundary resistance, while bulk (inner grain) resistance exhibits monotic temperature dependence. In addition, this unusual temperature dependence of the grain boundary resistance disappeared after the specimen was annealed in inert atmosphere. Based on all results, it is proposed that the atmosphere dependent grain boundary resistance was due to the depletion layer formed on the surface and along the grain boundary. This work conclude that even NASICON-type solid electrolytes is not stable in air.

11:00 AM ES04.08.09 Dense, Melt Cast Sulfide Glass Electrolyte Separators for All-Solid-State Li Metal Batteries Thomas A. Yersak, James R. Salvador, Nicholas P. Piesczonka and Mei Cai; Chemical and Materials Systems Lab, General Motors Global R&D, Warren, Michigan, United States.
According to consulting firm, Wood Mackenzie Power & Renewables, more than $500 million was invested in solid-state battery technology in 2018; double that of all previous years combined [1]. At the moment, it may be argued that sulfide solid-state electrolytes (SSEs) have the best combination of performance and manufacturability. Accordingly, ongoing work at General Motors Global R&D is concerned with the development of processing technology for sulfide SSE separators and evaluating how different processing methods affect SSE separator performance. In this presentation, we will compare the properties and performance of sulfide SSE separators made by cold pressing versus melt casting.

The manufacture of prototype bulk all-solid-state Li-ion batteries by a conventional slurry casting method has already been demonstrated [2]. However, the promise of doubling energy density with solid-state technology will only be realized with a Li metal anode. Unfortunately, the slurry cast/cold pressed separators used in all-solid-state Li-ion batteries may have upwards of 10 - 15 % porosity since they are analogous to green-tape ceramics. It has been shown that Li deposits penetrate porous cold compacted sulfide SSE separators, which results in cell failure by shorting [3,4]. Consequently, robust charging of bulk all-solid-state Li metal batteries is limited to elevated temperature and/or low C-rate.

LiF dopants have been shown to improve the resistance of cold-compacted sulfide SSE separators towards Li penetration [4]. However, Porz et al. suggest that dense sulfide glass SSE may fully block Li deposits [5]. The data presented here are the first to show, at a device scale, that dense sulfide glass SSE separators are effective at blocking the penetration of Li metal deposits. Monolithic glass wafers 4-5 cm² in diameter and 400-500 microns thick with a nominal composition of (Li₂S₀.6(Si₂S₆)₀.4(P₂S₇)₄) were made by melt casting. This glass composition was chosen as a compromise between glass formability and stability versus Li metal; the Si₂S₆ co-former reduced melt volatility while the P₂S₇ co-former increased the glass’ stability versus Li metal. Symmetric Li | SSE | Li cells were made to measure separator ionic conductivity and critical current density (CCD), the current density at which shorting failure is evident. The resulting melt cast glass had an ionic conductivity of 1.8 mS/cm and a CCD of 1,800 μA/cm² at room temperature. For comparison, porous separated formed by cold compaction of the same glass powder have an ionic conductivity of 0.81 mS/cm and a CCD of only 400 μA/cm² at room temperature. The lower conductivity of the cold compacted separator suggests that percolation and interparticle impedance of sulfide glass electrolytes is significant. Consistent with previous findings, the primary cause of shorting for the cold compacted separator was deposition of Li metal through interparticle porosity. On the other hand, the primary cause of shorting for the melt cast glass wafer was stack pressure induced macroracking and subsequent Li deposition through the crack. Our work suggests that dense sulfide SSE separators may prove appropriate for Li metal batteries so long as Li/SSE interfacial contact can be maintained at low stack pressures.

References:

11:15 AM ES04.08.10
Designing Polymer/Ceramic Composite Electrolyte for Solid–State Lithium Batteries Yuan Yang; Columbia University, New York, New York, United States.

Solid state batteries are attractive for next-generation energy storage as they could provide better safety and higher energy density. There are two major categories of solid electrolytes: ceramic electrolytes and polymer electrolyte. While ceramic electrolytes have high ionic conductivity, they have large interfacial resistance with electrode materials. On the other side, polymer electrolyte has low ionic conductivity, but compatible with state-of-the-art manufacturing process. An attractive approach is to combine polymer and ceramic electrolyte together to combine advantages of both. In this talk, I will discuss recent work in my group to enhancing performance of composite electrolyte-based solid state batteries, which includes 1) vertically aligned ceramic electrolyte in PEO Polymer electrolyte, which enhances ionic conductivity by more than a factor of 3, and reasonable density at which shorting failure is evident. The corresponding LiFePO4/Li cell can be cycled for over 400 cycles with high capacity retention. 2) stabilization of PEO with 4V layered oxide cathode. By optimizing surface coating and electrolyte composition, the cycle life is significantly improved compared to bare layered oxides.

References:

SYMPOSIUM ES05

Cooperative Catalysis for Energy and Environmental Applications
April 23 - April 25, 2019

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* Invited Paper

SESSION ES05.01: Heterogenous Catalysts
Session Chair: Huiyuan Zhu
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 122 B

10:30 AM *ES05.01.01
Metal-Support Cooperativity in Highly Dispersed Re Catalysts for Olefin Metathesis Susannah Scott¹, Fan Zhang², Mostafa Taoufik², Kai Szeto³, Régis Gauvin¹ and Laurent Delevoye;¹University of California, Santa Barbara, Santa Barbara, California, United States; ²CPE-Lyon, Lyon, France; ³Université de Lille, Lille, France.

Heterogeneous olefin metathesis catalysts are made by dispersing a mid-transition metal oxide on an "inert" support such as silica-alumina or alumina. However, the support is an essential part of the catalyst; no metathesis is observed in its absence. Moreover, the activity and stability of the catalyst depends strongly on the choice of support, including its
crystallinity and Lewis/Bronsted acidity. The origin of the cooperativity between support and active site was investigated by spectroscopic characterization of dispersed Re(VII) sites, including advanced NMR characterization methods. The number of active sites is limited by the availability of certain strong Lewis acid sites which are identified as five-coordinate Al centers. The lifetime of these sites is a function of their distance from hydroxyl groups, both terminal and bridging. A rapid deactivation process is attributed to the presence of local hydroxyls, while a slower deactivation process is associated with mobility of the active sites which brings them into proximity with hydroxyl groups. These insights allow us to design more effective metathesis catalysts with greatly improved activity and productivity.

11:00 AM ES05.01.02
Generation of Subnanometric Metal Species in Zeolites and Their Catalytic Applications
Lichen Liu and Avelino Corma; Instituto de Tecnología Química, Valencia, Spain, Spain.

Single metal atoms and metal clusters have attracted much attention thanks to their possibility as heterogeneous catalysts.[1,2] However, the generation of stable single atoms and clusters on a solid support is still challenging.[2] Recently, we report a new strategy for the generation of single Pt atoms and Pt clusters with exceptionally high thermal stability, formed within purely silicious MCM-22 during the growth of a two-dimensional precursor of the zeolite into three-dimensional structure.[4] These subnanometric Pt species are stabilized in the zeolite, even after treatment in air up to 540 °C. Furthermore, we have studied the dynamic structural transformation of those subnanometric Pt species during reduction-oxidation treatments and under reaction conditions (CO+O2, water-gas shift, NO+CO and NO+H2) by environmental transmission electron microscopy (ETEM).[5]

The Pt/MCM-22 was prepared by the transformation of 2D into 3D zeolite, using purely silicious H-ITQ-1 as precursor. In situ electron microscopy experiments were performed using a Titan 80-300 Environmental Transmission Electron Microscope at the Centre for Functional Nanomaterials (CFN), Brookhaven National Laboratory. Subnanometric Pt species are finely dispersed in MCM-22 crystals. With the help of aberration-corrected electron microscopy, we are able to directly measure the size of those Pt species and figure out their position in the zeolite. Some of the Pt atoms and clusters are located in the surface “cups” of MCM-22 and some of them are anchored to the zeolite framework. Nevertheless, a large part of subnanometric Pt species are located in the internal space of the structure, which is confirmed by the size-selective hydrogenation of propane and isobutane. The exceptional high stability of the encapsulated subnanometric Pt species has also been reflected in the propane dehydrogenation reaction to propylene, showing higher activity and stability than Pt nanoparticles prepared by conventional impregnation method.

Furthermore, using Pt@MCM-22 material as a model system, we have studied the evolution of Pt single atoms and clusters during reduction-oxidation treatments and under reaction conditions by ETEM. Pt nanoparticles and clusters will disintegrate into smaller clusters or even single atoms after calcination in O2. And single atoms and clusters will agglomerate into small particles after reduction by H2. Besides, it can be a general phenomenon that subnanometric metal species will undergo dynamic structural evolution under reaction conditions. For the same reaction, the states of metal species are dependent on the temperature and atmosphere. Our synthesis strategy can also be applied for preparation of Au@MCM-22 and Pd@MCM-22 materials, with subnanometric Au and Pd species encapsulated in MCM-22 zeolite. Those subnanometric metal clusters show unique catalytic behavior for selective aerobic oxidation of cyclohexane to KA-oil and low-temperature combustion of CH4, respectively.

Subnanometric metal species (single atoms and clusters with a few atoms) with exceptional high stability can be generated and stabilized in MCM-22 zeolite. Those subnanometric metal species show dynamic structural transformation during reduction-oxidation treatments and under reaction conditions and also show unique catalytic properties for various reactions.

References

11:15 AM ES05.01.03
Oxidation and Hydrolysis of Small Molecules and Organophosphorous Compounds via Thermal and Photocatalytic Pathways at Oxidation-Stable, Plasmonic Cu/TiO2 Aerogels

We stabilize plasmonic Cu nanoparticles by establishing extensive interfacial contact between photodeposited Cu and an anatase TiO2 aerogel support. The three-dimensional (3D) interfacial contact between sub-5-nm Cu nanoparticles and the covalently networked ~10-nm TiO2 particulates that create the aerogel framework stabilizes Cu against oxidation to an extent that preserves the plasmonic behavior of the nanoparticles, even after long-term exposure to ambient air. The Cu nanoparticles entrained in the TiO2 aerogel comprise a metallic Cu core with a shell featuring high fractions of Cu2+ and Cu3+ species, with a small fraction Cu+.

Both the plasmonic character and low oxidation-state speciation of Cu prove critical to several thermal and photochemical oxidation and hydrolytic degradation pathways. The Cu/TiO2 aerogels catalyze oxidation of carbon monoxide (CO) at temperatures as low as ~75 °C at rates comparable to those observed at nanostructured Au/TiO2 materials. Varying the relative amounts of Cu0, Cu+, and Cu2+ in the supported Cu nanoparticles determines the activation energy (Ea) for CO oxidation, with the lower oxidation states driving more efficaciously faster kinetics. In contrast, depositing Cu nanoparticles on commercial anatase powders results in Cu oxide nanoparticles with no detectable Cu+, and much higher fractions of Cu2+: Cu+ than observed when supporting Cu on TiO2 aerogels, resulting in poorer CO oxidation rates.

The Cu/TiO2 composite aerogels also fully hydrolyze the chemical warfare (CW) simulant dimethyl methylphosphonate (DMP) under aerobic and anaerobic conditions. In situ diffuse-reflectance infrared spectroscopy (DRIFTS) shows that all initial reactants and final hydrolysis products identified are bound to TiO2, however, aerogel-expressed anatase TiO2 alone does not hydrolyze DMPM. Excess surface concentration of OH species at Cu/TiO2 aerogels created near Cu/TiO2 junctions drives DMPM hydrolysis.

Finally, we describe the thermal and hydrolytic and oxidative degradation of the organophosphorous chemical warfare (CW) agents Sarin (GB) and Soman (GD) and the enhancement of their degradation by visible-light-driven photoelectrochemical oxidation of methanol under visible-light illumination, which is contrast is not observed for Cu photodeposited at non–networked anatase TiO2 nanoparticles.[1] The Cu/TiO2 aerogels enable us to apply a suite of thermal and photochemical degradation pathways for CW agent decontamination in one composite multifunctional material.

The exceptional activity for Cu-catalyzed oxidations and hydrolysis at a 3D Cu/oxide interface characteristic of aerogel supports highlights the importance of the interfacial design motif on both preserving plasmonic Cu and on driving oxidation and hydrolysis reactions in the dark—conditions requiring most of the promoting effects of the active support oxide to occur in very close proximity to the Cu/oxide interface.


11:30 AM ES05.01.04
Two-Dimensional Transition Metal Carbides as Supports for Tuning the Chemistry of Catalytic Nanoparticles for Effective Shale Gas Dehydrogenation
Yue Wu; Iowa State University, Ames, Iowa, United States.

Supported nanoparticles are broadly employed in industrial catalytic processes, where the active sites can be tuned by metal-support interactions (MSIs). Although it is well accepted that supports can modify the chemistry of metal nanoparticles, systematic utilization of MSIs for achieving desired catalytic performance is still challenging. The developments of supports with appropriate chemical properties and identification of the resulting active sites are the main barriers. Here, we develop two-dimensional transition metal carbides (MXenes) supported platinum as efficient catalysts for light alkane dehydrogenations. Ordered Pt/Ti and surface Pt/Nb intermetallic compound nanoparticles are formed via reactive metal-support interactions on Pt/Ti2C2T and Pt/Nb2CT catalysts, respectively. MXene supports modulate the nature of the active sites, making them highly selective toward C-H activation. Such exploitation of the MSIs makes MXenes promising platforms with versatile chemical reactivity and tunability for facile design of supported intermetallic nanoparticles over a wide range of compositions and structures. This work is recently published online at Nature Communications on December 10, 2018.
Fischer-Tropsch to olefins (FTO) synthesis has drawn significant attention due to the high demand of light olefins as building blocks for the chemical industry, the desire to reduce the dependence on petroleum cracking for these chemicals, and the need for improving environmental sustainability. Iron-based catalysts have emerged as promising FTO catalysts because of their low cost and excellent catalytic performance. We have designed a promising nanocatalyst of porous interconnected carbon nanosheets supported iron oxide nanoparticles for FTO synthesis. The catalysts demonstrate an extremely high iron time yield (FTY) of 1882 μmol/g cata./h with 41% selectivity for light olefins and excellent stability (>100 h time on stream). Our FTY value is found to be one of the highest FTYs and in particular, in 50 to ~1300 times higher compared with those catalysts exhibiting similar light olefins selectivity reported in literature. Mössbauer characterization demonstrates the presence of catalytically active iron carbide species after FTO reaction. *Ex situ* XAFS measurements reveal that the carbon nanosheets support stabilizes metallic iron during the initial catalyst reduction step, which leads to more carbon uptake under FTO reaction conditions to more efficiently form highly active iron carbide phase. In contrast, a control sample with carbon nanotubes as the catalyst support exhibits oxidized iron in the catalyst after removal from H₂ reduction pretreatment, suggesting a substantially reduced stabilizing effect of carbon nanotubes towards supported metallic iron nanoparticles. This results in inefficient formation of iron carbide species under FTO conditions. Additional XAFS results further confirm the buildup of iron carbide phase as a function of time on stream in the carbon sheets supported catalysts, whereas a much smaller portion and negligible growth of iron carbide phase was observed in the carbon nanotube supported catalysts under the same reaction conditions.

Electrocatalysts I

SESSION ES05.02: Electrocatalysts I

Session Chair: Shaojun Guo and Dong Su

Tuesday Afternoon, April 23, 2019

PCC North, 100 Level, Room 122 B

1:30 PM *ES05.02.01 Getting to the Core of the Matter—A Comparison of Core@Shell Nanocatalysts Built from Random Alloy and Intermetallic Seeds Sara E. Skrabalak; Chemistry, Indiana University - Bloomington, Bloomington, Indiana, United States.

Pt catalysts are widely studied for the oxygen reduction reaction (ORR), but their cost and susceptibility to poisoning limit use. A strategy to address both problems is to incorporate a second transition metal to form a bimetallic alloy; however, the durability of such catalysts can be hampered by leaching of non-noble metal components. Here, we show that random alloyed surfaces can be stabilized to achieve high performance and durability by depositing the phase on top of intermetallic seeds. Specifically, random alloyed PtCu shells were deposited on PdCu seeds that were either the atomically random face-centered cubic phase (fcc A1) or the atomically ordered phase (CsCl-like B2). Precise control over crystallite size, particle shape, and composition allowed for comparison of these two core@shell PdCu@PtCu catalysts and the effects of the core phase on electrocatalytic performance. Indeed, the nanocatalysts with intermetallic cores saw only an 18% decrease in activity after stability testing, whereas the random alloy core catalyst saw a 58% decrease. Although many random alloy and intermetallic nanocatalysts have been evaluated, this study is the first to directly compare random alloy and intermetallic cores for electrocatalysis and will facilitate the design of electrocatalysts with high activity and durability.

2:00 PM *ES05.02.02 Heterostructure Interface-Promoted Oxygen Electrocatalysis for Renewable Energy Applications Sen Zhang and Zhiyong Zhang; University of Virginia, Charlottesville, Virginia, United States.

Developing efficient energy storage and conversion devices with low environmental impact is central to our ability to secure the society’s energy and environmental sustainability. Oxygen electrocatalysis is the cornerstone for many renewable energy devices, including PEM fuel cells, metal-air batteries and water electrolyzers. In this talk, I will highlight the critical role of heterostructure interfaces in exploiting and optimizing the kinetics of oxygen electrocatalysis: oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline and neutral electrolytes. Associated with the formation of abundant oxide/sulfide interfaces over mixed spinel oxide nanosheets, the catalyst’s oxygen binding energy can be effectively tuned to enhance the OER and ORR activities, as revealed by the density functional theory (DFT) calculations. In 0.2 M phosphate buffer solution (PBS), the sulfurred zinc oxide present an excellent oxygen electrocatalytic activity and stability, with much lower OER and ORR overpotentials than single component oxide or sulfide, and with negligible performance decay in accelerated durability testing. As a result, it can be used as air electrode for both neutral/alkaline rechargeable zinc-air batteries. The relevant theoretical calculation, wet-chemical synthesis and structure/electrochemical analysis will be discussed.

2:30 PM *ES05.02.03 Ethanol Electro-Oxidation Using Pt3Sn Nanoparticles Yifan Liu and Chao Wang; Johns Hopkins University, Baltimore, Maryland, United States.

Direct ethanol fuel cell (DEFC) is a promising electrochemical energy conversion device. Its application, however, is hindered by lack of efficient catalysts for complete oxidation of ethanol into carbon dioxide. Here we report the study of ethanol electro-oxidation on Pt3Sn alloy nanoparticles. Electrochemical studies and product analysis were conducted comparatively on Pt3Sn/C, commercial Pt/C as well as Pt3Sn/C with surface tin species removed via KOH treatment. Our investigation reveal the dual role of Sn in Pt3Sn/C for ethanol electro-oxidation: surface SnOx species facilitate oxidation of *CHx to *CO while subsurface Sn species enhances oxidative removal of *CO.

2:45 PM *ES05.02.04 Tuning Hybrid Low-Dimensional Nanostructures for Efficient and Selective Electrochemical Reduction of Carbon Dioxide Sehmos Ozdemir1, Tristan Asset1, Samuel Garcia1 and Plamen Atanassov2,1; 1 Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2 Department of Chemical and Biological Engineering, The University of New Mexico, Albuquerque, New Mexico, United States; Department of Chemical and Biomolecular Engineering, University of California, Irvine, Irvine, California, United States.

The ability to directly produce fuels by consumption of carbon dioxide (CO₂) is one of the promising solutions that would have a transformational impact on both global energy and environmental sustainability. The success of this groundbreaking technology depends on products that form from consumption of CO₂, and hence it is important to develop effective catalytic materials for facilitating the CO₂ conversion process. However, existing catalysts do not exhibit high efficiency and good selectivity, which is leading to multiple products. Major reported CO₂ reduction catalysts are limited with formation of CO and formate that is two-electron reduced products. The formation of hydrocarbon products, which involve multiple proton and electron transfers still remain one of the major scientific challenges that needs to be addressed. Presently, there is no known catalyst that can facilitate CO₂ conversion to hydrocarbon fuels with both good efficiency and high selectivity mainly because of the little mechanistic understanding. Here, we will discuss tuning the hybrid structure of metal-oxide nanoparticles and two-dimensional (2D) layered materials as an efficient and selective CO₂ reduction electrocatalyst with the density functional theory calculations, which reveals the unusual electrocatalytic properties of hybrid structure creating intrinsic chemical and electronic coupling and assist to understand the mechanism beyond the process.

3:00 PM BREAK

3:30 PM *ES05.02.05 Synthesis of Novel Two-Dimensional Nanomaterials for Electrocatalysis Hua Zhang; Nanyang Technological University, Singapore, Singapore.

In this talk, I will summarize the recent research on synthesis and characterization of two-dimensional nanomaterials in my group, which include graphene-based composites, transition metal dichalcogenide (TMD)-based composites, single- or few-layer metal dichalcogenide nanosheets and hybrid nanomaterials, the large-amount, uniform, ultrathin
metal sulfide and selenide nanocrystals, and other 2D nanomaterials, nanodots prepared from 2D nanomaterials, etc. Then I will demonstrate the applications of these novel 2D nanomaterials in electrocatalysis.

4:00 PM ES05.02.06
Formation of CoO4/Co2O3 Heterolayered Nanotubes Electro catalysts for Efficient Oxygen Evolution Bocheng Qu and Yang Chai; The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Electrochemical splitting water into hydrogen and oxygen provides alternative way to reduce the current reliance on fossil fuels and thereby mitigate net carbon dioxide emissions.[1] The oxygen evolution reaction (OER) in water splitting process typically requires noble-metal-based catalysts to reach the desired current density of 10 mA cm–2 with a substantial overpotential.[2] Unfortunately, the high overpotential to drive the reaction significantly reduces the conversion efficiency of water splitting. Furthermore, it is difficult to fabricate these precious metal catalysts in mass production owing to their high cost and low elemental abundance. To solve these problems, considerable efforts have been devoted to explore low-overpotential, stable and earth-abundant OER catalysts. Given that transition metal compounds, including oxides, sulfides, phosphides, and nitrides, inevitably transform into their corresponding oxides after OER,[3] the transition metal oxides are the most promising alternatives owing to considerable stability and theoretical activity. In particular, cobalt oxide (Co3O4) holds great promise to substitute for rare precious metal based catalysts due to its low cost and earth abundance. However, the utilization of Co3O4 as an OER catalyst is limited by poor mass-transfer ability. Co3O4, with the flexible switch between Co2+ and Co3+ oxidation states, shows reversible surface oxygen ion exchange, high oxygen-storage capacities, and good electronic/ionic conductivity,[4] which offers the opportunity to generate strong electron interactions with other materials. Therefore, Co3O4 is expected to modulate the electronic structure and adsorption property of Co3O4 effectively.

We develop heterolayered CoO4/Co2O3 nanotubes catalysts by using Cu2O nanowires as templates. The CoO4/Co2O3 nanotubes exhibit superior activity for oxygen evolution in comparison with pristine Co3O4 nanotubes. Our density functional theory (DFT) calculations show that CeO2 can systematically modulate charge density of Co3O4, which provides near-optimal adsorption energies at Co catalytic sites for various OER intermediates simultaneously, and substantially enhances OER performance of Co3O4. This work underscores the importance of modulating the electron density of catalytic sites, and provides the guidance to implement more targeted strategies for developing highly efficient OER catalysts.


4:15 PM ES05.02.07

Given the crucial role of catalysis science in our society, understanding how to design catalyst structures for desired catalytic activity and selectivity becomes a grand challenge. Core-shell nanostructured materials hold the promise of being active, cost-effective, and stable catalysts. I will demonstrate how we understand the structure-performance correlation at the atomic-scale level through a set of computational approaches and apply it to address the catalyst challenge in the fields of energy conversion and storages. Computationally, we designed heterostructured perovskites for electrochemical water splitting, which were experimentally synthesized, characterized and validated(Figure 1). This sets the stage for the future design of core-shell oxide nanoparticles and their use for chemical reactions under harsh chemical environments. I will provide an understanding of the activation mechanism of the heterostructures based on first principle simulations (Figure 2). Finally, I will bridge core-shell architected oxide and transition metal systems and discuss our vision of potential design strategies.


SESSION ES05.03: Poster Session I: Electro catalysts
Session Chair: Huiyuan Zhu
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES05.03.01

Many researchers are eager to achieve novel systems for the synthesis of fuels or organic substances from CO2 under solar irradiation in an effort to help alleviate global warming and fossil fuel shortages. If CO2 can be reduced by utilizing water as an electron donor, then this would constitute an ideal reaction that would mimic photosynthesis in plants. We have previously reported CO2 reduction with very low overpotential and high reaction selectivity in an aqueous medium using abundant manganese complex polymer ([Mn-McN]2) catalysts.[1] Moreover, as a catalyst for oxygen evolution reaction, we have developed akaganeite-type iron oxyhydroxide surface-modified with amorphous nickel hydride (β-FeOOH:Ni/a-Ni(OH)2).[1-3] In this presentation, we demonstrate photocathodeelectrochemical CO2 reduction to CO with a solar-to-chemical conversion efficiency (ηCO2) of 3.7% by combining the earth-abundant catalysts wired with a cheap poly-crystalline silver photovoltaic cell (poly-Si cell) as a light absorber. Over 80% of current efficiency for CO production was observed in a one-compartment reactor, even in the presence of both oxygen gas and protons. We have also successfully conducted the reaction in neutral aqueous solution by formation of a Ni(OH)2/NOH redox system by pre-treatment of the β-FeOOH:Ni/a-Ni(OH)2. A photocathode composed of [Mn-McN] and triple junction amorphous silicon connected with a β-FeOOH:Ni/a-Ni(OH)2 anode also achieved ηCO2 of 1.0%, which suggests a future possibility to realize an ultimately-simplified monolithic artificial photosynthesis device to produce only gaseous products through the use of earth-abundant catalysts and a photosorbber.[4]

References
Interface engineering is one of the important schemes to optimize the intrinsic electronic structures of electrocatalysts and thus enhance the activity of the oxygen redox reactions for the applications of energy conversion devices such as fuel cells and metal-air batteries.\(^{(1)}\) When two different materials come to contact, charge transfer takes place at the interface due to the discrepancy between two Fermi levels. As a result, the excessive charge would boost the ORR process.

In our work,\(^{(2)}\) we take Mn-based mullite and perovskite as the prototype oxides to examine the interface tuning effect on the ORR performance. It is known, for individual either mullite or perovskite, only very limited ORR performance could be achieved.\(^{(3)}\) But, fundamentally, for Mn-based mullite, it contains two different crystalline fields,\(^{(3)}\) i.e. the Mn-centred pyramid\((3)-1\) and octahedral\((-4). The pyramid field \((\text{Mn}^{3+})\) introduces the \(d^{2}\) unit occupancy in the Fermi level region, which results in the ORR catalytic activity. For the octahedral field, it does not satisfy the requirement of the \(e_g\) unit occupancy. Thus, only one type of Mn is utilized. In order to maximize the active sites Mn, it is insightful to convert partial Mn\(^{3+}\) to Mn\(^{4+}\) to increase the \(e_g\) orbital occupancy. Through interfacing with n-type perovskites with higher Fermi levels, electrons will transfer to mullite side and achieve the conversion of Mn\(^{4+}\) to active valance Mn\(^{3+}\).

Based on the above arguments, we synthesized the heterogeneous catalysts, \((\text{AMn}_x\text{Mn}_y\text{O}_{z}\text{A}=\text{Ca, Sr, Ba, }x=0-0.5), i.e. \text{Mn-based mullite oxide interfacing with the IIA-group perovskies}, via the facile one-step co-precipitation method. We do find that the mixed-phase oxides display higher ORR performance. Among the three perovskites (\(\text{AMn}_x\text{Mn}_y\text{O}_{z}\text{A}=\text{Ca, Sr, Ba}), Ba-perovskite ultimately causes the band bending of mullite and thus leads to the highest half-wave potential \(-0.79\text{ V (vs. RHE)}\) in regards to individual mullite and Ba-perovskite, boosted by the accumulated electrons distributed in the mullite side at the interface. This work provides a strategy to rationally design the heterogeneous electrocatalysts via interface engineering.

References:

ES05.03.04
Redox Polymer Mediated Electrochemistry of Oxygen Reduction Reactions
Arneet Rajput, E. C. Montoto and Joaquin Rodriguez-Lopez; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Achieving high theoretical energy densities in alkalai metal-air batteries is still practically limited and is an inefficient process.[1] The low performance of these batteries is a result of combination of unwanted side reactions and the consequent formation of precipitates on the electrode surface. These discharge products, in turn, passivates the electrode surface and reduces the discharge capacity of the alkalai battery.[2] Two use of solution-based catalysts in systems such as lithium-oxygen batteries have been reported to drive the formation of precipitates away from the electrode. This results in the enhancement of energy density and cyclic stability of batteries.[2, 3] In recent years, redox-active polymers (RAPs) have gained vast interest because of their multiple redox active sites. This nature of RAPs can be employed for multi-electron mediation. In our laboratory, we are currently investigating RAPs as potential oxygen reduction catalysts in different alkalai metal-air batteries. Our electrochemial results represent the mediating property of RAPs and demonstrate their electro-catalytic performance, specifically in regard to substrate and ion type. These results are coherent with the ability of RAPs to tune mechanism via conformation.[4] Nevertheless, we are still limited on the kinetic information of these poly-electrolyte systems.

In this report, we will present the redox and catalytic behavior of RAPs in different alkalai-air environments. Additionally, voltammetric simulations will be presented for understanding kinetic mechanisms involved at the electrode interface and in the polyelectrolyte solution. We present the voltammetric simulations of polyelectrolyte behavior for different electrolyte concentrations and ions. These simulations provide a deeper insight on feasible chemical pathways and the complex kinetics involved in this system. In summary, our studies aim to investigate and expand the horizon of RAPs-mediated electrochemistry for interfacial protection and to study further interfacial charge transfer reactions.

References:
species embedded into carbon-based networks are efficient active species for the OER. In this work, we developed a hybrid ORR catalyst through the coordination of Co-based organometallic molecules to N-doped multiwalled carbon nanotubes (MWCNTs). Notably, our method offers a room-temperature reaction pathway for the formation of a stable catalytic complex through the exploration of N-doped structures. The hybrid ORR catalyst shows excellent catalytic performance with an onset potential of 0.95 V (RHE), superior durability, and good methanol tolerance. Chemical and structural characterization after many reaction cycles reveals that the Co-based organometallic species maintained the original structure of cobalt(II) acetylacetonate with coordination to the carbon-based materials. Also chemical and morphological characterization demonstrate after many reaction cycles reveals that a molecular well-dispersed active species at the surfaces of the carbon-based materials.

ES05.03.06
Synthesis of Ultrathin Wall CuO Nanotubes for CO Oxidation Yiwei Yu1, Na Ta1, and Jingyue Liu1; 1School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; 2Department of Physics, Arizona State University, Tempe, Arizona, United States.

Ultrathin nanostuctures with ultrathin walls provide readily accessible, high specific surface area for heterogeneous catalysis and sensing applications [1]. We report here the development of a room temperature synthesis process that produces tubular CuO nanowires with ultrathin wall (<10 nm). The synthesis process consists of using pre-formed Cu nanowires as templates, rapid annealing to oxidize the outside layers of the Cu nanowires, and a final well-controlled electrochemical corrosion process to obtain the final tubular structures. Characterization of the fabricated tubular structures by XRD and electron microscopy revealed that the morphology of the tubular structure conforms to the template Cu nanowires and that the crystalline tubular structure consists of CuO single phase. The synthesized CuO nanotubes have an average inner radius of 29 nm, outer radius of 35 nm and wall thickness ranging from 4 nm to 9 nm. After conditioning of the fabricated CuO nanotube catalyst during the first cycle of low temperature CO oxidation it demonstrated high activity with 100% CO conversion at 150°C in the following cycles, probably due to in situ reconstruction of the nanotube surface structures. The activation energy, stability and the structural evolution of the CuO nanotube catalyst during low temperature CO oxidation will be discussed [2].

[2] Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research. The authors acknowledge the use of facilities within the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University

ES05.03.07
Nickel-Containing Species Molecularly Immobilized on the Carbon Nitride as Hybrid Electrocatalysts for the Oxygen Evolution Reaction Sujin Seok, Dawoon Jang, Sunghee Park and Sungjin Park; Inha University, Incheon, Korea (the Republic of).

Water electrolysis is a type of oxygen electrochemistry that has been studied as a sustainable and effective energy conversion and storage device. The reaction occurring at the cathode electrode of the water electrolysis is referred to as HER (hydrogen evolution reaction), and the reaction occurring at the anode electrode is referred to as OER (oxygen evolution reaction). The OER reaction is slow because of the four-electron reaction, which is a major cause of the efficiency degradation. There is a need to develop new catalysts that allow the OER reaction to occur rapidly.

Precious metal oxides such as IrO2 and RuO2 exhibit great electrocatalytic activity for OER in acidic and alkaline conditions. However, because of high cost and scarcity of the precious metal elements, cost-effective and Earth-abundant metals, such as Fe, Co, and Ni. Among them, Ni-containing materials, show excellent electrocatalytic performances in alkaline medium.

Carbon materials are applied to various fields such as catalytic reaction, adsorption reaction, battery, and energy storage material. It has been known that bonding of nitrogen to such carbon materials can improve the properties of carbon materials, and much research has been conducted. Among them, carbon nitride (g-C3N4) is what we made in this experiment. In the case of C3N4, the synthesis method is simple and not toxic, and it has a band gap of about 2.7 eV, which is applied in various fields. Particularly, in the case of the most stable form of C3N4, graphitic carbon nitride (g-C3N4) is attracting attention as a catalyst which does not use metal as a material having a two-dimensional structure.

Hybrid catalytic materials containing single atoms or molecule-based active species fixed on nano-materials have been suggested as advanced catalyst for various reactions. In this study, we compared the OER performance of Ni-C3N-x (x = 10, 30, 50, 70, 100, 200) according to the composition of g-C3N4 and nickel. Novel hybrid system consisting of molecularly dispersed Ni-based materials on a g-C3N4 framework show excellent electrocatalytic performance for the OER.

We concentrated on Ni-C3N-200 because it shows the best catalytic performance for the OER. Chemical analysis revealed that Ni-C3N-200 contained Ni-based molecular species that were not aggregated in the porous g-C3N4 network and did not interfere with the network structure of C3N4. As calculated using BET data, the pore size of Ni-C3N-200 powder was 70 nm of diameter and surface area of Ni-C3N-200 was found to be 25.7 m2/g. EXAFS analysis investigated the local structure around Ni, Ni-C3N-200 shows the main peak at 1.6 A indicating the presence of Ni-N bonds.

In addition, electrochemical characterization results suggest dispersed Ni-containing molecular entities are active species for the OER. The Ni-C3N-200 sample exhibits the best electrocatalytic activity with an onset potential of 1.54 V (vs. RHE), which is less positive by 80 mV relative to g-C3N4. Not only the reduced onset potential, but also the kinetics, of the OER is enhanced by the attaching of the Ni-containing species on C3N4. The corresponding tafel slopes of IrOx, Ni-C3N-200, Ni-C3N-100, g-C3N4, and pristine GCE are 86, 60, 88, 230, and 470 mV/s, respectively. In test duration, the CV curves after 500 and 1000 cycles were almost like the initial curve and the chronoamperometry (CA) shows Ni-N bonds.

ES05.03.08
Fabrication and Photocatalytic Activity of Noble Metal(Ag, Au) Coated Fe3O4@TiO2@Fe3O4@TiO2 Nanomaterials Jin-Seung Jung; Gangnung-Wonju National University, Gangnung, Korae (the Republic of).

With the development of industrial technology, the amount of organic pollutants is constantly growing. In particular, water pollution produced by printing and textile factories has seriously affected the environment and caused severe consequences, such as aesthetic pollution, toxicity, and perturbation of aquatic life. Recently, with growing demand for clean and comfortable environment, purification technologies with high efficiency and low cost to reduce the pollutants of wastewater are urgently needed. Heterogeneous Fe3O4@TiO2@Au,Ag nanocomposites have an average inner radius of 29 nm, outer radius of 35 nm and shell thickness of 25 nm. The Fe3O4@TiO2@Au,Ag nanocomposites can be easily collected by applying external magnetic field due to the magnetic property of core Fe3O4 particles. The noble metal(Au,Ag) coated Fe3O4@TiO2@Au,Ag nanocomposites exhibited high photocatalytic activity in the degradation of rhodamine B (RhB) and methylene blue (MB) under visible light. The Fe3O4@TiO2@Au,Ag nanocomposites possess a relatively large specific surface area induced by noble metal(Au,Ag) nanoparticles, magnetic behavior for easy reuse, and enhanced photocatalytic efficiency caused by metal-semiconductor charge transfer or energy transfer. The increased photocatalytic activity of the Fe3O4@TiO2@Au,Ag nanocomposites is related to the increase in the electron–hole separation, caused by the interparticle charge transfer or energy transfer between TiO2 and noble metal(Au,Ag). The photodynamic process of TiO2 rapidly generates reactive oxygen species (ROS) as for instance superoxide anion radical (O2−), hydrogen peroxide (H2O2), singlet oxygen (1O2), and hydroxyl radical (OH). Thus, detection methods and generation mechanisms of the intrinsic reactive oxygen species (ROS), in photocatalysis, were surveyed comprehensively. The renewable photocatalytic activity of the photocatalyst was also examined.

ES05.03.09
Theoretical Study and Atomic-Scale Synthesis of Pt/Mn2 Interface for Bifunctional CO Oxidation Bin Shan and Rong Chen; Huazhong Univ of Science and Technology, Wuhan, China.

CO oxidation is a widely used model system for understanding fundamental aspects of heterogeneous catalysis. While platinum (Pt) continues to be a reference material for CO oxidation catalysis, poisoning of Pt catalysts presents a critical issue that blocks reaction sites and impedes subsequent reaction steps. Fabrication of CO poison-free Pt catalysts remains a great challenge due to its co-phile nature. Hence, we conduct a theoretical study of a bifunctional Pt/Mn-trimer interface that can effectively eliminate the CO poisoning effect. The Pt/Mn2 trimer structure is demonstrated irrespective of Pt cluster’s size, which can provide spatially separated sites for CO adsorption and O2 dissociation.
The binding strength of CO at the interfacial Pt sites is in the optimal range due to the charge transfer from Pt clusters to oxide, while the stronger polarization of Mn dimers induced by Pt clusters with stable three-dimensional morphologies can lower the energy barrier of O2 dissociation. Aroused by our theoretical results, we have synthesized the proposed structure via atomic layer deposition that tightly anchors subnanometer Pt clusters onto SmMn2O3 mullite facets, and with cluster configurations modulated by controlling key deposition parameters. Superior CO oxidation activity is observed with room temperature light off and turnover frequency rivaling the best in its class. The in-situ diffuse reflectance infrared Fourier transform spectroscopy analysis and oxygen isotope experiments confirm that the Pt/Mn2 structure’s activity originates from the bifunctional Mn2 components providing active oxygen atoms sources.

ES05.03.10
Ternary MnO/CoMn Alloy@N-Doped Graphitic from Bi-Metal Pigment for Bifunctional Electrocatalsis
Chen Deng; The University of New South Wales, Sydney, New South Wales, Australia.

Developing highly efficient bifunctional electrocatalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is of great importance in fuel cells and metal-air batteries. Among all candidates, non-precious transition metal composite materials with appropriate components and nanostructures might be promising for ORR and OER. Herein, we synthesized a composite containing CoMn alloy coated with N-doped carbon and MnO by a facile strategy of annealing Prussian blue analogues (PBA). The derived heterogeneous composite Mn2Co3-900 includes the merits of CoMn alloy, N-doped carbon and MnO, showing a low onset potential of 0.91 V, positive half-wave potential of 0.76 V and large limiting current density of 5.8 mA cm-2 among controlled samples. We proposed the enhanced ORR activity attributed to the optimal surface electronic configuration of alloy beneficial to dissociate intermediates and heterojunctions favoring charging transfer from alloy and oxide. In addition, this catalyst also shows promising activity for OER with onset potential of 1.53 V and low potential of 1.65 V at 10 mA cm2. This work therefore highlights the importance to construct alloy and oxide composite catalysts for superior electrocatalytic reaction.

ES05.03.11
An Etching-Assisted Route for Fast and Large-Scale Fabrication of Non-Layered Palladium Nanosheets
Yaming Liu; Xi’an Jiaotong University, Xi’an, China.

To date, great progress has been made in the shape-controlled synthesis of noble-metal nanocrystals. However, there still exists a major gap between academic studies and industrial applications due to the inability to produce nanocrystals in large quantities while retaining their uniformity. To help fill this gap, herein, we provide a new route to scale up and accelerate the production of non-layered palladium nanosheets (Pd NSs) by incorporating etching while retaining effective capping during the synthesis. The key to this rapid synthesis is the etching induced by selected etchants (e.g., Fe3+/Fe2+, Cl2/O2, Br2/O2, and F2/O2). Specifically, this synthesis can be accomplished within 3 min, reaching a yield as high as 7.2 g L−1 h−1. The thickness of Pd NSs can be tuned to 1.6, 2.0, 2.3, and 3.5 nm by controlling the etching and reducing rates via choosing different type of etchants. Moreover, these non-layered Pd NSs are fabricated in an aqueous solution without the addition of any organic compounds; therefore, the surface of these NSs is extremely clean. When used as a catalyst for the formic acid oxidation reaction, the as-prepared non-layered Pd NSs exhibit a mass activity as high as 1350 mA mg−1, which is 3.7 times higher than that of commercial Pd/C, due to their much larger electrochemical surface area (66.2 m2 g−1, which is 2.7 times higher than that of commercial Pd/C).

ES05.03.12
Creation of Controllable High-Density Defects in Silver Nanowires for Enhanced Catalytic Property
Chaoqi Wang; Xian Jiaotong University, Xi’an, China.

Noble metal nanocrystals with planar defects (e.g., twins, dislocations, stacking faults, and grain boundaries) symbolize a rising family in heterogeneous catalysts. It is of great importance to control surface terminations of planar defects of noble metal nanocrystals to play the significant role in their catalytic activity. However, there are still great challenges in preparation for noble metal nanocrystals with controllable high-density defects.

Here, we demonstrate a unique approach to the creation of Ag nanowires with high-density surface terminations of planar defects through controllable nanoparticles coalescence in one-dimensional pores of mesoporous silica. The density of defects can be easily adjusted by tuning the annealing temperature during synthetic process. The high-density defects promote the adsorption and activation of more reactants on the surface of Ag nanowires during catalytic reactions. As a result, the as-prepared Ag nanowires exhibit enhanced activities in catalyzing dehydrogenative coupling reaction of silane in terms of apparent activation energy and turnover frequency (TOF). We show further that the silane conversion rate can be enhanced by maximizing the defect density and thus the number of active sites on the Ag nanowires, reaching a remarkable TOF of 8288 h−1, which represents the highest TOF that has been achieved by far on Ag catalysts. The adsorption tests have further demonstrated the enhancement of the catalytic activity can be ascribed to the improved adsorption of reactants. This work not only proves the important role of surface terminations of planar defects in catalysis but also provides a new and general strategy for constructing high-density defects in metal catalysts.

ES05.03.13
Atomic-Resolution In Situ Observations of Metal-Support Interactions on Nanostructured Pt/CoO Catalysts
Joshua L. Vincent and Peter Greuter; Arizona State University, Tempe, Arizona, United States.

In reactions involving gas-solid interactions on nanostructured supports, the distinction between catalytically significant atomic structures and unreactive spectators is obscured by the variety of surface states that exist under reaction conditions. Studies of catalysts with well-defined support morphologies could assist in limiting the scope of structural configurations under consideration. Cerium dioxide (CeO2), a technologically important redox catalyst owing to its aliovalent behavior, can be synthesized into nanocrystalline cubes and rods; cubes surface-terminate with [100] planes, while rods surface-terminate with [110] and [100] planes [1]. Density functional theory (DFT) calculations indicate that CeO2 (100) surfaces are less stable than [110] surfaces, which suggests that cubes should be more reactive than rods [2]. However, for the CO oxidation reaction, rods are reported to be more active than cubes [1, 3], which is consistent with our results.

No atomic-resolution, in situ information exists for the surface structures or metal-support interfaces that occur on CeO2 rod/cube-supported catalysts, so we may only speculate upon the origin of the rods’ superior activity. This study employs ex situ and in situ environmental transmission electron microscopy (ETEM) to uncover the cooperative interactions that give CeO2 rod-supported catalysts enhanced catalytic activity. The CO oxidation reaction (CO + 1/2 O2 → CO2) will be employed as a probe for catalytic activity, due to its chemical simplicity and relevance to clean energy conversion. Nanostructured CeO2 cubes and rods will be synthesized through established hydrothermal methods [1], and Pt nanoparticles will be loaded onto them through conventional impregnation methods. A quartz tube reactor coupled to a gas chromatograph will be used to determine turn-over frequencies and activation energies for the catalyst, informing the reaction space to be explored during environmental transmission electron microscopy (ETEM) experiments. We expect that a Mars van Kevelten-of mechanism regulates activity in these catalysts, which would suggest that highly dynamic interfacial structures are likely to be catalytically significant. To this end, aberration-corrected ETEM (AC-ETEM) will be used to visualize the dynamic atomic structures that form in reaction conditions. The structures at the metal-support interface - and the dynamics that occur there - will be compared amongst the different types of interfaces that are observed (for example, Pt/CoO interfaces formed from Pt supported on CeO2 [100] vs. CeO2 [110] planes) [4].

[4] We gratefully acknowledge support of NSF grant CBET-1604971 and the use of facilities at Arizona State University’s John M. Cowley Center for High Resolution Electron Microscopy.
Tuning the Outcome of CO as the Intermediate

To address this challenge for science and the imagination often draw inspiration from the biological process of photosynthesis that powers our biosphere and supplied the fossil fuels global economies rely on. In this context, the active sites of enzymes have inspired researchers to develop molecular complexes that capture key environmental and functional principles of nature’s catalysts. However, not all aspects of biological energy transducing systems are or should be targets of chemical mimicry in designing an artificial photosynthesis, and some of the more favorable properties associated with solid-state heterogeneous catalysts have motivated molecular based surface-modification strategies. In this presentation, I will discuss efforts from our research group to develop heterogeneous–homogeneous architectures that combine the form factors of their underpinning solid-state supports with molecular coatings, enabling cooperative control and tunability of physical properties.1–6


8:45 AM *E0504.03 Tuning the Outcome of CO2 Reduction via Cooperative Interactions Between Bismuth Electrodes and Electolyte Cations Joel Rosenthal; University of Delaware, Newark, Delaware, United States.

Bismuth-based materials can promote the electrocatalytic reduction of CO2 to a variety of high energy density products depending on the conditions employed. For example, Bi cathodes promote the reduction of CO2 to CO with fast kinetics and high efficiencies in the presence of imidazolium ([Im]+) based cations. The Bi/[Im]+ systems can drive the electroreduction of CO2 to CO with Faradaic efficiencies and current densities of FE = 90 % and jF = 5–25 mA/cm2, respectively at applied overpotentials of ~300 mV. By contrast, when in the presence of [DBU–H+] based electrolytes, Bi cathodes promote the conversion of CO2 to formate (FE = 80 % at jF = ~45 mA/cm2) via an orthogonal 2e− reduction process. These studies reveal that variation of the electrolyte cation is a viable strategy to tune CO2RR with bismuth cathodes. We have undertaken a multipronged effort to understand how the cooperative interactions between polarized bismuth electrodes and electrolyte cations dictate the products of CO2 reduction. Through a combination of electroanalytical and computational methods along with advances analyses that include XANES, EXAFS and X-Ray reactivity experiments, we demonstrate that the Bi/[Im]+ and Bi/[DBU–H+] interfaces are not static. Under conditions at which CO2 electrolysis takes place, the bismuth materials undergo significant compositional and structural changes that are all believed to be important to the activity and selectivity of these systems for CO2RR. The mechanistic pathway(s) by which bismuth electrodes undergo potential-dependent chemical and structural transformations is dependent on cooperative effects between the electrode/electrolyte and manifest in the catalytic plasticity that is displayed by these Bi[cation] assemblies. Implications for future development of catalyst/electrolyte combinations that can efficiently promote CO2 conversion will also be discussed.

9:15 AM E0504.04 Electrochemical Reduction of Aqueous CO2 to Synthesis Gas Using β-PdH Wenchao Sheng; Tongji University, Shanghai, China.

Electrochemical reduction of CO2 (CO2RR) to value-added chemicals and liquid fuels using off-peak electricity or renewable energy is a green approach for energy storage and carbon cycling. The Faradaic efficiency and selectivity of CO2 reduction remain very low due to the very high energy barrier for CO2 activation. However, co-production of H2 and CO from the CO2RR aqueous electrolysis is appealing because H2 and CO with appropriate ratios as the synthesis gas can be used for methanol synthesis or Fischer-Tropsch reactions. Pd has been found to generate H2 and CO with a ratio between 1:1 and 2:1, which is in contradiction to the fact that Pd is prone for CO poisoning. In situ X-ray absorption spectroscopy and X-ray diffraction spectroscopy studies reveal that Pd has transformed into β-PdH under the electrochemical reduction conditions of CO2RR. Density functional theory calculations suggest that in situ formed β-PdH is not subjected to CO poisoning, and therefore the active species for the CO2RR.

9:30 AM E0504.05 Sequential Cascade Electrocataylsis Converts Carbon Dioxide to C-C Coupled Products Gourav Gourav1,2 and Joel W. Ager1,2; Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 1School of Materials Science and Engineering, University of California, Berkeley, California, United States.

Inspired by nature’s use of multiple enzymes to produce multi-carbon products from CO2 and sunlight [1], it is attractive to consider analogous cascade catalysis schemes in electrochemical CO2 reduction to achieve higher selectivity than is possible now with conventional metal electrocatalysts [2]. Cascade catalytic processes perform multi-step chemical transformations without isolating the intermediates. Here, we demonstrate a sequential electrocatalytic cascade to convert CO2 to C2 hydrocarbons and oxygenates using CO as the intermediate [2]. CO2 to CO conversion is performed by using Ag and further conversion of CO to C-C coupled products is performed with Cu. Temporal separation between the two reaction steps is accomplished by situating the Ag electrode upstream of the Cu electrode in a laminar flow cell. Convection-diffusion simulations and evaluation of the electrodes individually were performed to identify optimal conditions for cell operation. With the upstream Ag electrode poised at -1 V vs RHE in a flow of CO2-saturated water in aqueous carbonate buffer, over 50% of the CO is further converted to C-C coupled products (ethylene, ethanol, propanol) on the downstream Cu electrode held at -1.2 V vs RHE. By independent control of the electrodes, control over hydrogenation and oxygenates selectivity is achieved, with increasing CO activity at the Cu electrode increasing the FE to C2 oxygenates. Additionally, by supplying CO as well as CO2 to downstream electrode, mass transfer of reactants is increased, which allows for higher CO2 reduction currents compared to single electrode controls.


Carbon dioxide utilization will play a critical role as the community aims to reduce the levels of atmospheric carbon dioxide. While 10% of current CO₂ emissions can be converted directly into fuels, the transformation of CO₂ into useful chemical feedstocks can account for another 7%. One central example of CO₂ utilization is the addition of CO₂ to cyclic epoxides, generating cyclic carbonates, a polymer precursor. This reaction is characterized by the attack of a Lewis acidic metal on the epoxide to activate it toward CO₂ insertion. This reactivity has been demonstrated by many metal organic framework scaffolds. The Morris group recently synthesized a new class of metal organic frameworks termed VPI-100-M. The MOFs incorporate a tetra-azaamacyclic and are competent catalysts for the aforementioned reaction. Herein, a detailed mechanistic study of the interactions between the VPI-100 analogs (Zr and Hf) and substrates of interest is presented. The implications of these results on the mechanism of catalytic action are discussed and placed in the context of the MOF catalytic field. The node appears to play a minor role during catalysis, as the dominant interacting center was determined to be the metalloccyclam via both quartz crystal microbalance studies and calculations. In contrast, the node appears to dominate the CO₂ sorption properties of the MOF. Therefore, there is a synergetic effect between the linker and the node imparting enhanced reactivity.

10:45 AM ES05.04.07
Nanoporous Au-Sn with Solute Strain for Simultaneously Enhanced Selectivity and Durability During Electrochemical CO₂ Reduction Lihua Qian and Xianglong Lv; Huazhong University of Science and Technology, Wuhan, China.

Electrochemical carbon dioxide (CO₂) reduction on metallic catalysts suffers from the restricted selectivity and the competition with hydrogen evolution, which sensitively depend on ambiguous contributions of strain state and alloying in bimetallic catalysts. Herein, nanoporous Au-Sn (NPAS) containing trace tin solute into Au lattices is delicately designed to convince real strain effect, while rule out the other disturbing factors, such as alloying, crystal facets and surface composition. In comparison with nanoporous Au, the NPAS with a solute strain of ~2.2% enables the efficient CO₂-to-CO conversion, being 92% at -0.85 V versus reversible hydrogen electrode and retains the activity for at least 8 hours. Simultaneous enhancements of selectivity and durability stem from the shifted d covalent band that might change adsorption energy of key intermediate *COOH, and sluggish Au surface diffusion onto the strained ligament against coarsening, respectively.

11:00 AM ES05.04.08
Strain As an Axis to Tune Selectivity in Electrochemical CO₂ Reduction Taewoo Kim and David Fenning; University of California, San Diego, San Diego, California, United States.

Electrochemical recycling of CO₂ to high-valued carbon-based products such as hydrocarbons and alcohols offers not only mitigation of greenhouse gas emissions but also the opportunity to use CO₂ as a medium to store energy. Copper is a promising electrocatalyst for CO₂ reduction, capable of producing such products with reasonable activity. However, poor product selectivity results in low energy efficiency – a critical challenge. In this study, we apply tensile strain to planar Cu catalysts and demonstrate the ability to direct the aqueous CO₂ reduction reaction toward particular products, indicating that we can manipulate the binding energy of key intermediates via strain. We observe that the magnitude of the tensile strain applied to the planar Cu catalysts strongly governs the CO₂ reduction selectivity. At overpotentials where higher reduction products are favored, the strongest tradeoff is between formation of CO and CH₄. This tradeoff indicates a change in CO binding energy, one of the key descriptors of CO₂ reduction to hydrocarbons and oxygenates. These findings provide evidence for strain engineering as a tunable approach to modifying the surface binding energy of CO₂ reduction intermediates and offer a practical experimental approach to identifying favorable strain states. We will describe our latest understanding of the changes in surface chemistry that strain introduces, offering insights to tailor the design of high surface-area electrocatalysts with enhanced selectivity for CO₂ reduction.

11:15 AM ES05.04.09
Functional Nanogluels for Robust Single-Atom Catalysts Xu Li¹,², Jia Xu¹, Jie Zeng² and Jingyue Liu¹; ¹Arizona State University, Tempe, Arizona, United States; ²University of Science and Technology of China, Hefei, China.

Recent advances in catalysis by supported single metal atoms have demonstrated that single-atom catalysts (SACs) can be highly active and selective for a variety of important catalytic reactions. The key challenge to practical applications of SACs is, however, the stabilization of high number density of single metal atoms dispersed onto high-surface-area supports during the desired catalytic reactions. Unless they are strongly anchored by defect sites supported metal atoms are thermodynamically unstable, especially at elevated temperatures and under reducing environment. The use of nanogluels, commonly practiced in industry to anchor metal nanoparticles, provides an alternative approach to confining the movement of supported single metal atoms during catalytic reactions. We recently demonstrated a novel strategy to anchor supported Pt single metal atoms by using CoO₂ clusters (1-2 nm) as nanogluels. The synthesis processes consist of dispersing CoO₂ clusters onto inexpensive and high-surface-area SiO₂ supports and then depositing Pt atoms onto the CoO₂ clusters. We used CO oxidation as a probe reaction to evaluate the stability of the Pt/CoO₂/SiO₂ SAC. The results demonstrate that not only the CoO₂ clusters stabilized the Pt single atoms during the CO oxidation but they also significantly enhanced the activity, presumably due to the redox capability of CoO₂ clusters that facilitate CO oxidation. Our strategy is general and can be extended to other types of functional nanogluels to develop robust SACs for a variety of catalytic transformation of important molecules.*

*This research was funded by the National Science Foundation under CHE-1465057. We gratefully acknowledge the use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

11:30 AM ES05.04.10
Robust and Synthesizable Photocatalysts for CO₂ Reduction—A Data-Driven Materials Discovery Arunima Singh¹, Joseph Montoya², John M. Gregoire¹ and Kristin A. Persson; ¹Physics, Arizona State University, Tempe, Arizona, United States; ²Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³California Institute of Technology, Pasadena, California, United States.

The photocatalytic conversion of the greenhouse gas CO₂ to chemical fuels such as hydrocarbons and alcohols continues to be a promising technology for renewable generation of energy. Major advancements have been made in improving the efficiencies and product selectivity of currently known CO₂ reduction photocatalysts, nonetheless, materials discovery is needed to enable economically viable, industrial-scale CO₂ reduction. We report here the largest CO₂ photocathode search to date, starting with 68860 candidate materials, using a rational first-principles computation-based screening strategy to evaluate synthesizability, corrosion resistance, visible-light absorption, and compatibility of the electronic structure with fuel synthesis. The results confirm the observation of the literature that few materials meet the stringent CO₂ photocathode requirements, with only 52 materials meeting all requirements. The results are well validated with respect to the literature, with 9 of these materials having been studied for CO₂ reduction, and the remaining 43 materials are discoveries from our screening that merit further investigation.

SESSION ES05.05: Photocatalysis
Session Chairs: Jingyue Liu and Bilge Yildiz
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 122 B

1:30 PM ES05.05.01
Robust Single-Atom Catalysts for Energy and Environmental Applications Jingyue Liu, Jia Xu, Yang Lou, Yafeng Cai and Xu Li; Arizona State University, Tempe, Arizona,
The rapid advances in catalysis by supported single metal atoms are clearly manifested by the explosive growth of journal publications on this research frontier in the last few years. Single-atom catalysts (SACs), defined as those catalysts that consist of only isolated metal atoms dispersed onto an appropriate support, have demonstrated unparalleled selectivity and/or significantly enhanced activity for a variety of important catalytic reactions including gas- and liquid-phase, electrocatalytic, and photocatalytic reactions. From the materials science perspective, we can view the active sites of SACs as surface dopants or anchored impurities which modify the surface electronic structure of the support material. From the homogeneous catalysis perspective, we can view the active sites of SACs as metal centers coordinated by a rigid ligand of the solid support; the specific coordination environment depends on the anchoring site of the metal single atom. The catalytic performance as well as the stability of SACs strongly depend on the support material and the electronic atom-support interactions. Strong metal atom-support interactions usually involve charge transfer or formation of covalent bonds which can significantly modify the physiochemical properties of the metal atoms and consequently their adsorption properties for reactant molecules. Since we do not have much freedom to tune the properties of single atoms support (surface) engineering or functionalization becomes the central research theme in the field of catalysis by supported metal atoms. In this presentation, we will discuss the recent strategies in anchoring metal atoms to high-surface-area supports, key catalytic reactions that demonstrate the excellent selectivity/activity on SACs, challenges to commercial applications of SACs, and perspectives for developing robust SACs for energy and environmental applications.

This research was funded by the National Science Foundation under CHE-1465057. We gratefully acknowledge the use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

2:00 PM ES05.05.02
Does Polaronic Self-Trapping Occur at Anatase TiO₂ Surfaces? John J. Casey and Keith McKenna; University of York, York, United Kingdom.

The behavior of electron and hole charge carriers at surfaces of titanium dioxide (TiO₂) controls performance for important applications including photocatalysts and solar cells. While anatase TiO₂ exhibits high electron mobility in the bulk a commonly held belief is that strong coupling between electrons and phonons can lead to electron trapping at anatase surfaces. However, direct evidence is scarce and the nature of the trapping sites and electronic properties remains unclear. To address this question we investigate the trapping of electrons and holes at low and high index surfaces of anatase TiO₂ using an accurate hybrid density functional theory approach. We find that, as in the bulk, electrons do not trap on the low index planes (001, 100, 110, 112) of anatase crystals. For the higher index planes (103, 105, 107) that contain structural step defects, we find that electrons do trap at the low coordinated Ti cations present on the steps. The trapping of holes at the surfaces of anatase TiO₂ is a more complicated picture, as the distribution of hole traps is facet dependent. 001 and 100 surfaces, as well as 105 and 107 surfaces which have 001 type terraces, have the strongest affinity to trap holes. Hole trapping for the 101, 110, 112 and 103 surfaces is found to be favoured in the sub surface layers and not at the surface facet. These results provide crucial insights into the behavior of electrons and holes in TiO₂ relevant for applications in photocatalysis and challenge the common perception that electrons trap at low index surfaces of anatase TiO₂.

2:15 PM ES05.05.03

Composite catalytic aerogels provide a highly flexible design motif for solar-fuels photocatalysis. This multifunctional platform enabled us to physically connect surface plasmon resonant (SPR)-driven visible-light sensitization, electron and ion transport, and oxidation and reduction catalysis within Au–TiO₂ aerogels—a single, hierarchical composite catalyst nanarchitetture [1].

Although Au–TiO₂ aerogels exhibit attractive properties for photocatalytic H₂ generation [1] and photochemical water splitting [2], quantum efficiencies at the globular ~5-nm Au guests remain low. Here, we focus on the challenge of enhancing SPR-driven visible light water oxidation in our composite aerogels. We introduce iridium oxide (IrO₂)-based co-catalyst nanoparticles into the plasmonic aerogels to enhance SPR-generated electron–hole pairs. We also describe a new synthetic strategy to vary the size of SPR-active Au nanoparticles in the Au–TiO₂ aerogel architecture to increase the efficiency of the SPR sensitization process. Ultimately, we wish to retain the connectivity of the sensitization, charge separation, and catalytic steps we previously demonstrated in our composite plasmonic photocatalytic aerogels and add in the high (as high as 20–50%) SPR-sensitized charge separation efficiencies reported elsewhere [3] to create a robust composite aerogel-based solar fuels photocatalyst delivering state-of-the-art photocatalytic efficiency.


2:30 PM BREAK

SESSION ES05.06/ES06.05: Joint Session: Cooperative Catalysis
Session Chairs: Wenchao Sheng and Jin Suntivich
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 122 B

3:30 PM *ES05.06.01/ES06.05.01
Mechanisms and Selectivity of the Electrochemical CO₂ Reduction Reaction on Multiple-Site vs Single-Site Catalysts Peter Strassner; Chemical Engineering, Technical University Berlin, Berlin, Germany.

Strategies for closing the anthropogenic carbon cycle using the chemical conversion of CO₂ into useful molecules have become a scientific and technological priority. Of all chemical ways to convert CO₂ into CO, oxygenates or hydrocarbons, the direct electrochemical coupling of water electrolysis and CO₂ reduction appears attractive, as it is a one-pot process step, occurs at ambient temperature and pressures, involves solely water and CO₂ as reactants, and may involve renewable electricity from wind, solar or hydro power plants.

The CO₂ electrode reaction is by and large carried out on the surface of metal catalysts. At industrially relevant current densities and electrode potentials, however, these catalysts typically suffer from low faradic C₃ product selectivities due to the competing, very fast reduction of water, i.e. the hydrogen evolution reaction. New catalyst concepts with tunable selectivity for hydrogen evolution versus CO₂ reduction are needed.

In this contribution, we share recent comparative experimental and computational mechanistic insight in the electroreduction of CO₂ on metallic multi-site versus molecularly inspired metal ion-N modified high surface area carbon single-site catalysts. We provide new insight into CO selectivity trends and put particular emphasis on the competing reaction pathways to methane and methanol. We show that carbon-based single site catalysts are an intriguing cost-effective alternative to their metallic rivals at industrial current densities.

4:00 PM *ES05.06.02/ES06.05.02
CO Oxidation on Supported Ir Single Atoms—Consequences of Strong CO Adsorption on Kinetics and Resting State of the Catalyst Ayman M. Karim; Virginia Tech, Blacksburg, Virginia, United States.
Supported single-atom catalysts provide an ideal system to study reaction mechanisms on a molecular level and to bridge heterogeneous and homogeneous catalysis. Single atoms have shown remarkably different activity and selectivity for several reactions, however for low temperature CO oxidation the reaction mechanism is not well understood and there is debate whether single atoms have higher intrinsic activity than nanoparticles. In this talk, the mechanism of CO oxidation on atomically dispersed Ir/MgAl₂O₄ catalysts will be presented and compared to that on nanoparticles. Using in-situ and in-operando DRIFTS and HERFD-XANES complemented by DFT calculations, we identified the active Ir single-atom complex, and resting state of the catalyst for low temperature CO oxidation. We provide evidence that strong CO adsorption on single atoms leads to an Eley-Rideal mechanism where Ir(CO) is the active complex (i.e. a CO ligand is present during the catalytic cycle). The results show that due to the ability of single atoms to coordinate with more than one ligand, strong adsorption by CO does not necessarily lead to catalyst poisoning. Additionally, we demonstrate that the unusual kinetics on single atoms can be used as a facile surface sensitive characterization tool for quantifying the number of single atom sites in catalysts containing a mixture of single atoms and nanoparticles. The results provide a new perspective for understanding reaction mechanisms and interpreting spectroscopic and catalytic activity of supported metal single atoms.

4:30 PM ES05.06.03/ES06.05.03 Oxide Bilayers as High Efficiency Water Oxidation Catalysts Through Electronically Coupled Phase Boundaries Jennifer Redig, Sanjay Mathur and Thomas Fischer; University of Cologne, Cologne, Germany.

New semiconductor metal oxides capable of driving water-splitting reactions by solar irradiation alone are required for sustainable hydrogen production. Whereas most metal oxides only marginally deliver the photochemical energy to split water molecules, uranium oxides are efficient photoelectrocatalysts due to their absorption properties ($E_g \approx 2.0 - 2.6 \text{ eV}$) and easy valence switching among uranium centers that additionally augment the photocatalytic efficiency. Although considered a scarce resource, the abundance of uranium compounds in the environment is manifested in the huge quantities of stored UF₆ gas, produced as waste streams in the nuclear fuel enrichment process. Here we demonstrate that thin films of depleted uranium oxide (UO₂) and their bilayers with hematite (α-Fe₂O₃) are high activity water oxidation catalysts due to electronically coupled phase boundaries. The electronic structure of uranium oxides showed an optimal band edge alignment in U₃O₈ and UO₂ which can be tuned by electron doping and the reaction mechanism is confirmed by theory. The enhanced photocurrent density of the heterostructures with respect to well-known hematite offers unexplored potential of uranium oxide in artificial photosynthesis.

4:45 PM ES05.06.04/ES06.05.04 Design of Supported Transition Metal Catalysts for Methane Partial Oxidation Darinka Prince¹,², Julie Fornaciari¹,², Adam Weber² and Alexis T. Bell¹,²; ¹Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California, United States; ²Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The abundance of methane and its low cost makes it an optimal raw material for chemical precursors and energy-dense fuels. Conventional synthesis of methanol involve a multistep process, which requires high energy input and high cost [1]. Alternatively, electrochemical methane oxidation using a catalyst is a promising single-step approach to achieve a direct conversion of methane to methanol at lower temperatures and cost [2].

An efficient catalyst needs to be developed for this energetically challenging process. The catalyst should be active for C-H bond activation, thereby enabling oxidative hydroxylation of methane, and simultaneously inhibit further methanol oxidation. To date, a variety of the catalysts, including supported metals (Pd, Ru, Au, Ag) and metal oxides (V₂O₅, Fe₂O₃, CoO, Mn₃O₄, MoO₃, CrO₃) have been tested in electrochemical cells and shown promise for this approach [2]. However, further systematic studies are essential for understanding the mechanism for methane oxidation and thereby enabling the rational design of the catalysts. In this regard, porous metal oxides and supported single-atom catalysts (SAC) are particularly interesting [3]. These catalysts show potential for high methane conversion and are ideal model catalysts to identify active sites and facilitate understanding of the reaction process at a molecular level. In spite of great interest; however, it still remains challenging to achieve atomically dispersed metals in high loadings for efficient catalysis.

In this study, a design of first-row transition metal oxides and MOF-derived supported single-atom catalysts will be presented. The catalysts are synthesized with wet-chemistry, and subsequently, characterized for electrochemical methane-to-methanol oxidation. Structural and chemical analyses of catalysts using a combination of various microscopic and spectroscopy techniques are used to establish structure/property relationship. These insights provide valuable basis for a scientific-guided approach toward new metal oxide and supported single-atom catalysts for this challenging process.


SESSION ES05.07: Poster Session II: General Catalysis
Session Chairs: Lichen Liu and Dong Su
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES05.07.01 Theory-Guided Sn/Cu Alloying for Efficient CO₂ Eletroreduction at Low Overpotentials Xuei Zheng and Yi Cui; Stanford University, Palo Alto, California, United States.

The electrochemical reduction of carbon dioxide (CO₂) to formate provides an avenue to the synthesis of value-added carbon-based fuels and feedstocks powered using renewable electricity. Unfortunately, high selectivity in formate electroreduction has thus far only been achieved at the expense of highly cathodic potentials, yielding impractically low power conversion efficiencies. In this work, we use density functional theory to investigate the effect of alloying Cu and Sn on the activity and selectivity towards formate. A theoretical thermodynamic analysis of the reaction energetics suggests that the incorporation of copper into tin could suppress hydrogen evolution and CO production, thus achieving high selectivity in formate electroreduction at lower potentials.

ES05.07.03 RuO₂-Loaded Black TiO₂ Nanotube Array Electrodes for Efficient Electrocatalytic Chlorine Evolution Reaction Deok Ki Cho and Jin Young Kim; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

TiO₂ nanotube arrays (NTAs) substrate has highly ordered nanostructure, which is able to provide numerous surface area. Ruthenium oxide (RuO₂) is successfully deposited onto TiO₂ nanotube arrays via electrochemical deposition. We simply alter electrochemical properties of TiO₂ nanotube arrays through changing annealing condition. It is shown that air-annealed TiO₂ NTAs substrate is a good support for hydrogen evolution reaction (HER) but not for chlorine evolution reaction (CER). Also, non-annealed TiO₂ NTAs substrate shows dissolution in acidic condition under high cathodic current. Thus, Ar-annealed black TiO₂ NTAs substrate is appropriate to use both hydrogen evolution and chlorine evolution. It has been found that the conductivity of the electrode under the anodic polarization is essential for achieving good CER performance, and the black TiO₂ has been found to be the best scaffold for the RuO₂ catalysis.
Graphene, an atomically thin two dimensional carbon allotrope with hexagonal lattice structures, has been intensively studied in recent years owing to its outstanding electrical, mechanical, thermal and optical properties. In particular, graphene, as a highly conductive material not only because of its densely packed structure but also because of its outstanding optical transparency and mechanical flexibility. This is particularly important for flexible organic devices as the performance of organic materials considerably degrades in the presence of water or oxygen molecules from ambient air. Inorganic materials such as silicon oxides (SiOx) and aluminum oxides (Al2O3) have been predominantly employed as the gas barrier films. However, the complicated fabrication processes as well as the poor mechanical flexibility of these materials have hindered the practical application to flexible electronic devices. In this regard, the excellent gas impermeability, flexibility, and transmittance of graphene films are expected to be useful for more reliable and durable operation of organic devices. Nevertheless, the defects in CVD graphene are unavoidable due to imperfect synthesis, etching, and transfer processes, which considerably degrades the barrier performance of graphene films. Thus, the characteristics and catalytic activity of cWONFs and CsWONPs were studied. However, neither material modified GCE was used, and the LOD was 56.0 nM within a linear range of 0–280 μM. The LOD obtained when using WONFs in electrochemical sensing is lower than that of CsWONPs. Furthermore, WONFs have intrinsic peroxidase-like activity and electrocatalytic properties. For colorimetric detection, we investigate their peroxidase-like activity which is turning from colorless to blue by catalyzing the oxidation of a peroxidase substrate, such as 3,3′,5,5′-tetramethylbenzidine, in the presence of H2O2.

**ES05.07.05**

Chevrel-Phase MoS2—A Platform for Probing Ensemble Effects on Selective Conversion of CO2 and CO to Methanol Over Metal-Promoted Sulfides

**Joseph Perryman**1,

Jessica Ortiz-Rodriguez2, Ambarish Kulkarni3, Christopher Patridge4 and Jesus M. Velazquez4; 1University of California, Davis, Davis, California, United States; 2Chemistry, D’Youville College, Buffalo, New York, United States.

Presented herein is an investigation of a promising Chevrel-phase metal sulfide catalyst that is capable of electrochemically converting CO2 to liquid and gas fuels such as methanol and hydrogen. When promoted by copper, extended structures of Chevrel-phase MoS2 clusters are capable of reducing CO2 to CO in aqueous electrolyte with an overpotential of -0.4 V vs RHE. H2 gas is simultaneously evolved during this process, contributing to total current densities as high as 35 mA/cm2. Methanol and formate are the only CO2 reduction products formed from electrolysis, although utilizing CO as a feedstock has been shown to mitigate parasitic current density toward formate production. Also presented is the formulation of an interesting electronic structure-function correlation founded on the basis of ex-situ and operando X-ray absorption spectroscopic analyses and corroborated by results of electrocatalytic evaluation as well as theoretical calculation.

**ES05.07.06**

Fe-Doped Ni3P on Stainless Steel for Efficient Oxygen Evolution at High Current Densities

**Lejuan Cai**1 and Yang Chai; 1Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China.

Clean hydrogen energy produced from water-alkali electrolyzers has shown great potential to replace current fossil fuels due to its carbon-neutral and sustainable nature.[1] Although high hydrogen evolution (HER) electrocatalytic water splitting performance has been achieved, the overall water splitting performance is still hindered by oxygen evolution reaction (OER) due to the sluggish four-proton-coupled electron transfer process.[2] In addition, the OER process is also essential for CO2 reduction reactions and plays dominant role in rechargeable metal-air batteries.[3] Thus, it is of great significance to develop effective electrodes for large-scale oxygen evolution at the minimum cost of electricity. From the perspective of practical water-alkali electrolysis, commercial water splitting requires an overpotential below 300 mV to realize high current density above 500 mA/cm2, superior long-term stability and cost-effective OER electrolytes.[4] Therefore, designing highly efficient OER electrodes based on non-noble metals is highly desirable for practical water splitting.

In this manuscript, we successfully fabricate self-supported Fe-doped Ni3P electrocatalyst on 304-type stainless steel (SS) mesh and realize first-class OER performance. The as-prepared OER electrode exhibits an overpotential below 300 mV (about 255 mV) to achieve high current densities of 500 mA/cm2, which meets the commercial water electrolyzer requirements and outperforms most of other state-of-the-art OER electrodes. Besides, extremely low Tafel slope and superior long-term stability are also achieved due to the highly active catalytic sites, great conductivity and strong adhesion between electrocatalyst and current collector. DFT calculation was then introduced to verify the robust OER performance of Fe-doped Ni3P. According to the theoretical results, Fe-doping brings about reduced adsorption energy of O-containing intermediates and improve the charge transfer from catalytic surface to intermediates, which is beneficial for intermediates activation and O2 evolution. More importantly, Fe doping can greatly improve the Fe2+/Fe3+ adsorption on oxidized Ni-Fe-P surface, leading to activated O2 species for enhanced OER performance. The combination of experimental and theoretical results deepens our understanding to the synergistic effect of Ni- and Fe-sites during OER process and provides significative guidance to design OER electrodes for practical water electrolysis.

Reference:


**ES05.07.07**

Hexagonal Tungsten Oxide Nanoflowers as Enzymatic Mimetics and Electrocatalysts

**Chan Yeong Park,** Hongil Jo, Juhyun Park, Kang Min Ok and Tae Jung Park; Chung-Ang University, Seoul, Korea (the Republic of).

Tungsten oxide (WOx) has been widely studied for versatile applications based on its photocatalytic, intrinsic catalytic, and electrocatalytic properties. Among the several nanostructures, we focused on the flower-like structures to increase the catalytic efficiency on the interface with both increased substrate interaction capacities due to their large surface area and efficient electron transportation. There are three keys to obtain the improved flower-shaped WOx (WONFs) with a large surface area. First is acidic environment (pH 1.6), seconds is the synthesis was conducted at a low temperature (to provide a low reaction rate), and last is high precursor concentration. Like hexagonal zinc oxide nanorods, hexagonal WOx crystals have been considered polar crystals with ± (0001) polar planes. These polar crystals are prone to grow along their polar directions (c-axis) at a low growth rate. The difference in crystal growth rate between the polar plane and nonpolar plane would produce anisotropic crystal growth. Another factor influencing the crystal morphology is the capping agent, which can selectively adsorb onto the preferred crystal planes and regulate the crystal growth rate. In this reaction system, NaCl can act as a capping reagent by adsorbing onto the crystal plane parallel to the c-axis of the WOx crystal nucleus. Moreover, Cs2WO4-based experiments were performed to investigate the influence of the NaCl on the overall crystal morphology and structure of the WOx nanoflowers, however, the resulting nanoparticles, Cs2WO4, were not flower-shaped and denoted as CsWONPs. The WONFs were compared with CsWONPs in terms of structural and catalytic properties. Therefore, improved WON, nanoflowers (WONFs) with large surface areas were developed through a simple hydrothermal method using sodium tungstate and hydrogen chloride solution at low temperature, without any additional surfactant, capping agent, or reducing agent. Structural determination and electrochemical analyses revealed that the WONFs have hexagonal Na0.33WOx, 0.17H2O structure. To verify the catalytic efficiency enhancement by the unique shape and structure of the WONFs, they were compared with calcined WONFs, cesium WOx nanoparticles, and other peroxide-like nanomaterials. The WONFs were characterized using a combination of experimental techniques, and it was found that WONFs have the largest surface area (51.936 m2/g) despite having a particle size larger than that of CsWONPs. Furthermore, WONFs have intrinsic peroxide-like activity and electrocatalytic properties. For color regeneration, a modified GCE was used, and the LOD was 56.0 μM within a linear range of 0–280 μM. The LOD obtained when using WONFs in electrochemical sensing is lower than that obtained when using WOFs in colorimetric detection. Additionally, the characteristics and catalytic activity of cWONFs and CsWONPs were studied. However, neither material exhibited both intrinsic peroxide-like activity and good electrocatalytic activity.
In heterogeneous catalysis, metal-support interactions can lead to enhanced catalytic performance. Cu and Pt nanoparticles supported on CeO$_2$, for example, are more active for CO oxidation than those supported on non-reducible metal oxides (such as SiO$_2$) [1]. The enhancement arises from CeO$_2$'s ability to locally donate oxygen at the metal-support interface, through a Mars van Krevelen-like mechanism. The ease with which oxygen may be removed from the CeO$_2$ lattice has been shown theoretically to depend on the atomic structure of the metal-support interface [2]. At present, though, there is little experimental data on the atomic structures that comprise the metal-support interface during catalysis. Correspondingly, many important questions remain as to what interface or proximal surface structures participate in or enhance interfacial oxygen transfer.

In the present study, we seek to elucidate the cooperative atomic-scale dynamics that occur at the metal-support interface during catalysis. The CO oxidation reaction (CO + $\frac{1}{2}$ O$_2$ > CO$_2$) will be employed as a probe for catalytic activity, due to its chemical simplicity and relevance to clean energy conversion. Nanostructured CeO$_2$ will be used as a model support, and Pt nanoparticles will be loaded onto them through conventional impregnation methods. A quartz tube reactor coupled to a gas chromatograph will be used to determine turn-over frequencies and activation energies for the catalyst, informing the reaction space to be explored during environmental transmission electron microscopy (ETEM) experiments. Abrerration-corrected ETEM (AC-ETEM) will be used to visualize the atomic structures that form in reaction conditions. Operando electron energy-loss spectroscopy will be implemented to track the gas composition during catalysis, allowing catalytic activity to be correlated directly with the observed surface and interfacial structures.

The results of these experiments will provide operando information on the interfacial and surface structures that correlate with activity for an important clean energy conversion reaction. These relationships are of fundamental interest to the heterogeneous catalysis community, and they may facilitate the engineering of highly active Pt/CeO$_2$ catalysts for the energy and environmental remediation applications where they are indispensably used [3].


ES05.07.10
Optimized Fabrication Process of Electrospun Nanofiber Film Using Circular Electrode for Multifunctional Filter Application

Dong Hee Kang, Na Kyong Kim, Liangjun Zheng and Hyun Wook Kang; Department of Mechanical Engineering, Chonnam National University, Gwangju, Korea (the Republic of).

Electrospinning technique is simple method to polymer based nanofiber film fabrication. Electrospun (ES) film is fabricated continuously stacked nanofiber that has porous structure. The porous characteristic of ES films permit their application in many fields such as textiles, filters, biomedical, drug delivery, energy, and sensors. Also, the electrospinning technique is readily adapted for the addition of micro and nanoparticles to provide specific functions in the mixing of the polymer solution. For further applications, the fiber diameter should be easily controlled by the electric field in the electrospinning, especially ES film based fiber application needs to have adequate fiber characteristics in uniformity, porosity and permeability. Traditional electrospinning using flat electrode for fiber collection has disadvantages to produce a ES film having a homogeneous thickness distribution. Also traditional electrospinning has difficulties in nanofiber film acquisition due to the deformation film layer in film detaching process. In this study, we investigate the electrospinning method using circular electrode for freestanding state nanofiber film fabrication. Freestanding ES film is possible to transfer layer by layer with film deformation through the repetition process. For the optimized freestanding ES film fabrication, numerical simulations are performed to analyze the electric field, equivalent polar, electric potential, and electrostatic pressure on the surfaces of the circle electrode collector in the electrospinning area. The electrostatic results explain the focusing phenomenon of freestanding films via ES fibers stacked on the surface of the 20 mm inner diameter circle electrode collector. Under the conditions with a 70 mm TCD and 12.5 kV, ES film is successfully fabricated on the top surface of the circular collector. After the optimization of ES film fabrication, PVDF/zeolite multilayer film fabricated by electrospinning with the circle electrode collector and repeated film transfer processes for the humidity removal test. Through the transferring process, the ES layers are laminated onto other film surfaces to fabricate a multifilayer. An ES multilayer film is composed with three-layer sandwich structure having a 2:5:2 volume ratio. The outer layers of filters I and II are ES layers of 15 wt% PVDF. The middle layers of filters I and II are 15 wt% PVDF and 18 wt% PVDF/zeolite (4:1) ES layers, respectively. The quantity of zeolite contained in the filter II multilayer is 17.2 μg. Filter I removes only 0.5% of the moisture with the film’s porous structure. In contrast, filter II absorbs 13.8% of the moisture from the humaid air. The zeolite particles embedded in the ES PVDF film capture moisture, which is absorbed to 15.1% of the weight of zeolite. As a result, freestanding ES film using circular electrode enables to functional multilayer for dust filtering, air ventilation and humidity removal.

ES05.07.11
Simulation of Realistic Dynamic NMR Spectra of Zeolites

Federico Brivio, Petr Nachtigall and Zdenek Tosner; Department of Physical and Macromolecular Chemistry, Charles University, Prague, Czechia.

Zeolites are crucial materials in fluid catalytic cracking. This process is of paramount importance in the production of fuel and other oil derivatives. Any improvement in their efficiency as catalytic compounds can hence lead to broad economic impact in this industrial sector, and general economy. The catalytic activity of zeolites is due to their crystalline micro-porous structure formed by interconnected alumino-silicate tetrahedra. This system of tetrahedra can be very complex and form several types of rigid frameworks where Si and Al can participate in different proportion. Frameworks can be further functionalized with the inclusion of other atomic species to tune their physical-chemical behavior.

Knowing the distributions of atoms in a given zeolite is hence crucial and can be investigated with means of nuclear magnetic resonance (NMR). Due to the critical role of Al atoms in catalytic process we focus on $^{27}$Al-NMR analysis. Experimental $^{27}$Al-NMR spectra are particularly difficult to interpret and obtain due to the quadrupolar moment of $^{27}$Al nucleus, but can return precious insight on the distribution of active catalytic sites usually associated with the Al atoms. Analysis of data can be supported by theoretical spectra obtained within ab-initio density functional theory (DFT) and the GIPAW formalism.

NMR signal is extremely sensitive to the atomic configuration and its chemical environment. Nonetheless, as far as we know, the large majority of theoretical investigations have compared experimental spectra to single specific structures assumed as representative of a whole system. This returns a partial, if not misleading, interpretation of the nature of the system, since different aspects, such as the dynamic of the system, or the measurement conditions, are overlooked.

To include such effects our study couples set of ab-initio Molecular Dynamics (AIMD) simulations with the calculation of NMR tensors of statistically significant (~100s) structures that occurs during the time evolution of the zeolites. This allows us to simulate realistic NMR spectra taking in account both dynamic effects and controlling the role on the NMR signal of different parameters such as temperature, pH, heterotomic substitution, hydration, …

The result of our study are then elaborated in collaboration with experimental group in order to compare our prediction with experimental spectra.

ES05.07.12
Photocatalytic Performance of Highly Transparent and Mesoporous Molybdenum-Doped Titania Films Fabricated by Templating Cellulose Nanocrystals

Yonghee Yoon, Soyoung Kim1, Cheolhwon Jeong1, Sunyong Lee1, Jaeyoung Kwon2 and Wonhee Lee1; 1Sejong University, Seoul, Korea (the Republic of); 2National Institute of Forest Science, Seoul, Korea (the Republic of).

In this paper, the synthesis of mesoporous Mo-doped titania films templated by cellulose nanocrystals (CNCs) and their photocatalytic performance are reported for the first time. The prepared titania composite precursors containing the CNCs and molybdanum chloride were spin-coated on indium tin oxide (ITO) glass substrate, followed by calcining at 400 °C for 1 h. X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and UV–vis spectrometer were employed to characterize the phase composition, pore structure, morphology, and optical properties of the titania films in relation to CNCs templating and Mo doping. Photocatalytic performances of the titania films were also evaluated on the photodegradation of trichloroethylene under a fluorescent light source. The Mo-doped titania films with CNCs templating were highly transparent and mesoporous, exhibiting only anatase phase, high specific surface areas ranging in 135.4 ~ 149.0 m$^2$/g, and small crystallite sizes of 9.5 ~ 11.1 nm. The results indicate that Mo ions
High energy density electrode materials are highly desired in the area of energy storage to satisfy the demands of modern society's development. The porous nature of the hybrid carbon materials and its micro-scale porous distribution is attractive in energy storage fields. Conjugated microporous polymer (CMP) was synthesized through coupling polymerization with the catalysis of noble metal. The porous width of CMP can be adjusted by different precursors, while the noble metal catalyst will remain in the porous CMP after polymerization. After pyrolysis of the CMP, the noble metal nanoparticles will be encapsulated in the carbon matrix. The noble metal nanoparticles encapsulated in carbon materials will show its synergistic effects in energy storage area and potential applications in other fields.

Pd Encapsulated porous carbon materials (Pd-PCMs) were prepared from the coupling polymerization of ary1 halide and aryl terminal acetylene, whereas Pd(PPh3)4 serves as both the catalyst in polymerization and the precursor of Pd encapsulated in Pd-PCMs. With its porous microstructure and encapsulated Pd nanoparticles among porous carbon materials, Pd-PCMs provide strong physical confinement and surface chemical interaction to improve the affinity of polysulfides to the carbon matrix. The capacity of the battery is 920 mAh/g after 200 cycles at rate of 0.3C. The application of Pd-PCMs in Li-S batteries has broadened the applications of CMP and its derivatives in the field of energy storage, and with different particles encapsulated in adjustable porous carbon materials, CMP and its derivatives will also show its potential applications in other fields like catalysis and environmental applications.

### SESSION ES05.08: Advanced Characterization I

#### 8:00 AM *ES05.08.01*

**Easy and General Synthesis of Large Size Mesoporous Metal Oxides**

Bishnu Bastakoti; North Carolina A&T State University, Greensboro, North Carolina, United States.

The synthesis of mesoporous materials has attracted great interest due to their wide range of applications in drug delivery, catalysis, sensors, photovoltaic cells, and fuel cells. Low-molecular weight surfactants have normally been used to synthesize mesoporous materials. In this study, a new strategy has been proposed to synthesize large size mesoporous metal oxides. The use of asymmetric triblock copolymers with core-shell-corona nanoarchitecture as a template and structure directing agent gives rise a wide variety of mesoporous materials with large mesopores (10-50 nm). The catalytic activity of large size mesoporous metal oxides towards oxidation of CO will be discussed.

#### 8:15 AM *ES05.08.02*

**High Energy Rechargeable Zinc-Air Batteries**

Zhongwei Chen; University of Waterloo, Waterloo, Ontario, Canada.

Development of low cost, high energy, safe and long-life energy storage systems is critical for widespread commercialization of smart grid and electric vehicles. Rechargeable zinc-air batteries have been considered as most promising candidates as energy storage system for transportation, smart grids and stationary power. They can display a considerably high specific energy (1218 Wh/kg) and volumetric energy density (6136 Wh/L). Besides their high energy densities, zinc-air batteries also demonstrate other desirable characteristics, such as abundant raw materials, environmental friendliness, safety, and low cost. The current zinc-air battery is typically composed of four main components: an air electrode, an alkaline electrolyte, a separator, and a zinc electrode. For the electrically rechargeable zinc-air battery, each main structural component faces its own challenges. In this presentation, I will present our recent work on advanced energy materials development for rechargeable zinc-air batteries by focusing on the novel zinc electrode, nanostructured bifunctional oxygen electro-catalysts, 3D bifunctional air electrodes, and solid-state electrolytes. More specifically, we will discuss: 1) how the 3D zinc-sponge electrode solve problems of zinc dendrite, shape change and passivation, 2) how the nanoengineered materials can enhance the catalytic activity and durability of oxygen electro-catalysts, 3) how the 3D air electrode architectures can advance the practical performance of the zinc-air batteries, and 4) how the novel solid-state electrolytes can sustain cell operation substantially longer than common aqueous alkaline electrolytes do, as well as their extended applications include portable, flexible, and diversely shaped zinc-air batteries.

#### 8:45 AM *ES05.08.03*

**Approximate Density Functional Theory for Computational Heterogeneous Catalysis**

Stephan Irle; Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The theoretical prediction of new catalysts requires precise knowledge of structural information on which to base accurate quantum chemical studies such as density functional theory (DFT) investigations of activation energies and reaction kinetics, often structural information is difficult to obtain, for instance when surfaces and nanoparticles undergo structural transformation under pretreatment and reaction conditions, exposing novel reactive sites responsible for the experimentally observed catalytic activity. A theoretical study based on ideal surfaces or particles created from bulk will entirely miss these important features, resulting in a theory-experiment disconnect.

The density-functional tight-binding (DFTB) method [1-5] is an approximation to DFT that reduces the computational effort by 2-3 orders of magnitude, and was used for the
prediction of the fullerene formation mechanism [6], the Haekelite formation mechanism on metal surfaces [7], the existence of a “sweet spot” for the catalyst oxygen content of carbon nanotube formation [8], and many other phenomena in materials sciences requiring highly complex quantum chemical modeling. The tremendous speed of the method originates from the careful parameterization of the Hamiltonian [9], eliminating all expensive integral evaluations. The method can deliver accuracy in structure and energetics comparable to DFT [4, 5, 10], and has recently been successfully employed in the pre-screening of reaction and activation energies for heterogeneous catalysis [11] and in the study of the topology of binary core-shell nanoparticles [12]. In this presentation we will highlight recent accomplishments in the parameterization effort related to the DFTB-based study of heterogeneous catalysis and illustrate the predictive capabilities in the context of graphene CVD synthesis on metal surfaces [13].

References:

9:15 AM ES05.08.04 Nanoscale Probing of Adsorbates on Catalyst Surfaces with Allof Beam Vibrational Electron Energy-Loss Spectroscopy Karthik Venkatraman1, Barnabé D. Levin1, Katia March2, Peter Rez3 and Peter Crozier1; 1School of Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States; 2EYing Materials Center, Arizona State University, Tempe, Arizona, United States; 3Department of Physics, Arizona State University, Tempe, Arizona, United States.

The ability to perform high-resolution mapping of adsorbate molecules or layers and correlate this with atomic structure would provide a transformative new tool for investigating the surface chemistry taking place on nanoparticles. Such a tool can be used to detect dissociative and non-dissociative sites on catalyst surfaces and study different bonding arrangements between the adsorbate and the catalyst. Electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) has been used for studying vibrational modes in materials with high spatial resolution and sensitivity [1, 2]. Radiation damage may be substantial when a STEM electron probe is placed directly on the adsorbate layer of interest. We adopt the allof beam EELS technique that makes use of the long-range Coulomb interaction between electrons and adsorbate molecules to minimize damage when the probe is placed just outside the adsorbate layer. The delocalized vibrational signal in the allof beam mode has allowed for probing variations in the amine content of graphitic carbon nitride photocatalysts [3]. A theoretical treatment of surface-enhanced EELS has also been given which explains the electromagnetic coupling between the adsorbate and catalyst to demonstrate enhancement of the vibrational signal from the adsorbate [4]. Here, we explore three classes of adsorbate/catalyst systems because of their simplicity and overall scientific importance and their suitability for developing the allof beam vibrational EELS technique, viz. PVP ligand shell on Au nanoparticles, CO on Pt nanoparticles supported on CeO2 nanocubes, and CO2 on Mo5 nanocubes.

All our results were obtained using a NION UltraSTEM 100 aberration-corrected microscope operated at 60 kV and equipped with a monochromator. Allof beam EELS from the PVP ligand shell/Au nanoparticle system suffers from a low signal-to-noise ratio (SNR) and consists of two weak and broad vibrational signals centered at 160 meV and 205 meV. These signals correspond to peaks associated with the C-N stretch, CH stretch, and C=O stretch modes as observed in the Fourier-transform infrared (FTIR) spectrum from pure PVP, convolved with the experimental energy-resolution [5]. Preliminary allof beam EELS results from CO on Pt (111) particles demonstrate that the “on-top” vibrational mode of CO at 260 meV can be detected from a monolayer of adsorbate, although the signal suffers from poor SNR. This is in qualitative agreement with the diffuse reflectance infrared Fourier-transform spectrum (DRIFTS) from the CO on Pt/CeO2 system. Allof-beam EELS from the CO2 on Mo5 system showed that the Mo5 surface was hydrated before chemisorption of CO2, which led to the formation of a bicarbonate species on the surface. Further vibrational EELS results to investigate the bonding arrangements at different crystallographic surfaces in all three systems will be presented.

References:
[6] The support from National Science Foundation CHE-1508667 and the use of (S)TEM at John M. Cowley Center at Arizona State University is gratefully acknowledged.

9:30 AM ES05.08.05 Pocket-Like Active Sites of Rh/MoS2for 100% Selective Hydrogenation of Crotonaldehyde Yang Liao1, Yongping Zheng2, Xu Liu2, Kyongjae Cho2 and Jingyue Liu1; 1Arizona State University, Tempe, Arizona, United States; 2University of Texas at Dallas University, Dallas, Texas, United States.

Selective hydrogenation of unsaturated aldehydes to saturated alcohols is extremely valuable for synthesis of fine chemicals but is a major challenge. We here report that single Rh atoms anchored on the edges of 2D MoS2(Rh/MoS2) can efficiently unsaturated crotonaldehyde to crotyl alcohol with 100% selectivity via steric confinement effect. The Rh/MoS2single-atom catalyst (SAC) is not only 100% selective but also active at moderate reactions conditions with a turnover frequency (TOF) of crotonaldehyde of 26.4/h at 80 °C (H-pressure is 5 bar). To our knowledge, the TOF of Rh/MoS2SAC is more than 50 times higher than that of the other reported heterogeneous catalysts that provides 100% selectivity for hydrogenation of crotonaldehyde to crotyl alcohol. Atomic resolution electron microscopy and CO-DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) results suggest that the Rh atoms strongly anchored to the edges of the Mo5sheets creates, resulting in unique electronic properties. The DFT calculations suggest that the edge anchored Rh can facilely dissociate H molecules to H atoms which spill over to form OH groups on the oxidized Mo edge sites of the Mo5sheets. The OH group and the associated Mo atom on each side of anchored Rh atom form a pocket-like active site with the configuration of HO-Mo-Rh-Mo-OH, in close resemblance of pocket-like sites of enzymes. Such specifically configured active sites impose severe steric hindrance that limits the possible adsorption configurations of the crotonaldehyde molecules and thus guide the chemical reaction to 100% selectivity. The strategy we used to construct pocket-like active site configurations is general and can be broadened to develop highly selective catalysts for a variety of important catalytic transformation of molecules [1].

[1]This work was supported by the National Science Foundation under CHE-1465057. The authors acknowledge the use of facilities within the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University. This research was funded in part by the International Energy Joint R & D Program (No. 20168510011350) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Knowledge Economy, Korean government.

9:45 AM ES05.08.06 Synergistically Enhanced Hydrogen Evolution Activity by Ni3S2 Nanocluster Decoration on Vertically Aligned MoS2 Thin Films for Efficient Solar Water Splitting Seokhoon Choi, Changyeon Kim, Ki Chang Kwon, Kootak Hong, Jun Min Suh and Ho Won Jang; Seoul National University, Seoul, Korea (the Republic of).

Hydrogen emerges as a next-generation clean energy source to replace fossil fuels. One of the most promising ways to produce hydrogen is photoelectrocatalytic (PEC) water splitting in which sunlight-illuminated photoelectrodes generate electrical current to transform water into useful hydrogen. However, the existing photoelectrodes such as Si with noble catalysts still suffer from low efficiency and poor stability. Moreover, the extremely high cost of the noble metal catalysts limits the wide use of water splitting photoelectrodes. Recently 2-dimensional transition metal disulfides (2D TMDs) have been attracted much attention as promising candidates to replace Pt, because 2D TMDs such as molybdenum disulfide (MoS2) and tungsten disulfide (WS2) have inherently large surface-to-volume ratios and possess high densities of catalytically active sites for hydrogen evolution reaction (HER). Herein, we demonstrate that large-area (12 cm x 12 cm) and transferable MoS2 thin-film catalysts with vertically aligned layers, which maximally
expose the edges on the thin film surface. The vertically aligned domains in the transferable MoS
thin films not only facilitate the charge transport toward reaction interfaces, but also maximize the exposure of active edge sites of MoS
. Furthermore, the Fe-doped NiS
(Fe: NiS
) nanoparticles (NPs) grown on the vertically aligned MoS
(v-MoS
) thin films are obtained by in situ growth during the synthesis of v-MoS
. The synthesized Fe: NiS
/v-MoS
 thin films exhibits only 105 mV at 10 mA/cm
2 for HER with exceptionally low Tafel slope of 66.6 mV/dec among the thin film type catalysts. Moreover, the Fe:NiS
/v-MoS
/p-Si heterostructure photocathode can provide the high photocurrent density of 25 mA/cm
2 in the measurements in reversible hydrogen electrolyte. Density functional theory (DFT) calculations further reveal that the constructed coupling interface between v-MoS
 and Fe:NiS
 facilitates the absorption of protons (H
+ ), consequently enhancing the catalytic activity of the Fe:NiS
/v-MoS
 thin film catalyst. Such outstanding performances indicate that the unique structure suggests a novel approach for designing advanced 2D materials-based electrocatalysts.

10:00 AM BREAK

10:30 AM *ES05.08.07
Atomic Resolution In Situ and Operando Characterization of Cooperative Catalysts
Peter Crozier; School for the Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States.

The functionalities associated with many thermochemical and photochemical catalysts rely on a variety of different materials properties which regulate and control electron, ion and hole transfer across surfaces, interfaces and three-phase boundaries. Developing a fundamental understanding of these processes requires an atomic level picture of the structure and bonding during reactions. The interactions between different components of the catalytic system can be explored with aberration corrected imaging and spectroscopy in a transmission electron microscope (TEM). The critical surface motifs that convert reactants into products may form only under reaction conditions and must be investigated with in situ or operando approaches (1, 2). Here we show how advanced imaging and spectroscopy can be employed to elucidate the functionally important features for a variety of catalysts. One strategy for addressing the problems associated with storage of solar energy is to generate solar fuels. Photocatalytic splitting of water to generate hydrogen is extremely challenging systems must be able to harvest light and transfer electrons/holes to suitable reaction sites at the surface. Carbon nitrides have bandgaps in the visible and are promising materials for hydrogen evolution (3). The domain size and location of the Pt co-catalyst nanoparticles on the surface plays a critical role in interfacial charge transfer and the overall H
2 production efficiency. Interfacial sites may also play an important role in light harvesting. For example, TiO
2 which usually only harvests UV light, can be functionalize to absorb in the visible by depositing thin layers of CeO
2. Moreover, the Fe:Ni co-catalyst nanoparticles on the surface plays a critical role in interfacial charge transfer and the overall H
2 production efficiency. Interfacial sites may also play an important role in light harvesting. For example, TiO
2 which usually only harvests UV light, can be functionalize to absorb in the visible by depositing thin layers of CeO
2.

References:

11:00 AM ES05.08.08
MoS
2 Supported Gold Nanoparticle Catalysis of CO to CO
2: William C. Coley and Amirali S. Akhavi; UCR, Morgan Hill, California, United States.

Transition metal dichalcogenides (TMDs) such as MoS
2 have technological application from chemical catalysis to emerging microelectronic integration. At the same time gold nanoparticles have demonstrated catalytic properties that differ from bulk gold depending on the substrate and particle size. We have indication that there may be catalytic states on gold nanoparticles supported by MoS
2 that allow for the room temperature binding of CO. We have shown with XPS the retention of CO and subsequent its removal with O
2. This may open up the potential to convert CO to CO
2 and methanol to higher order hydrocarbons such as ethanol. The MoS
2 is grown on a SiO
2 layer on a silicon wafer. We then deposit the gold nanoparticles by using e-beam deposition onto our MoS
2.

11:15 AM ES05.08.09
Spectroscopy of Ultrathin Bilayer Silicate Films on Pd(100) and Pd(111)
: Samuel A. Tenney, Veronica Lee, Jeffry A. Kelber and Dario Stacchiola; 1University of North Texas, Denton, Texas, United States; 2Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States.

In this talk we present the first reported photothermal infrared (PTIR) spectra of ultrathin bilayer silicate films with a spatial resolution better than 10nm and compare this with traditional infrared reflection absorption spectroscopy (IRRAS) of the same surface. The growth of ultrathin bilayer silicates on Pd(100) and Pd(111) is demonstrated under a variety of conditions and was observed in real-time with an in-situ low energy electron microscope (LEEM) and micro-low energy electron diffraction (μ-LEED). The bare Pd(100) and Pd(111) surfaces are fluid-like at the crystallization temperature of the silicate film as evidenced by the movement of the steps and terraces on the Pd surfaces. After crystallization of the silicate film was observed with LEEM and μ-LEED the samples were further characterized with X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), IRRAS and PTIR. The resolution of the infrared peaks from the nanoIR instrument are substantially better than those obtained from the traditional IRRAS setup owing to the significantly smaller sampling area. The PTIR spectra are overlaid with the topographic information obtained from the AFM tip and some hyperspectral images will be presented. The chemical activity and selectivity of these model silicate/Pd catalysts will be discussed.

11:30 AM ES05.08.10
Controlling the Concentration of Oxygen Vacancies in CeO
2-ZrO
2 Nanoparticles via Spatial Tailoring of the Active Site
Behnam Safavinia, Yumang Wang, Smiti Sahu, Jared Larrihueeri, Kerry M. Dooley and James A. Dorman; Louisiana State University, Baton Rouge, Louisiana, United States.

According to Environmental Protection Agency, over 55% of NO
x emissions in the US is caused by automobile exhaust and also resulting in the formation of CO
2 and hydrocarbon residues. Transition metal doped CeO
2-ZrO
2 (CZO) nanoparticles (NPs) are extensively employed in three-way catalysis due to their ability to adsorb and release oxygen helping to prevent coking. These CZO NPs have shown a 5.3 mW/mg catalytic activity comparable to state of the art catalysts utilized in dry reforming of methane. However, the activity of these structures under reaction conditions, which is function of the position of the active site (Ni), has been shown to reduce the oxygen storage capacity and increase coking over time. To address this, the current work aims to understand the structural and electronic properties of the active site of CZO NPs, allowing for an in-depth study of the formation of oxygen vacancies in the lattice due to the position of the active site.

In this work, a two-step process, co-precipitation/molen salt synthesis (MSS), has been explored for a CZO-Ni catalyst, comparing its catalytic activity to oxygen vacancy concentration to a standard prepared by sol-gel technique. Transmission electron microscopy and X-ray diffraction identify that the as-synthesized NPs are monodisperse spheres, with 10 nm mean diameter, exhibiting floccular phase. The concentration of oxygen vacancies in these NPs was studied using Raman spectroscopy, which shows a higher intensity defect-induced (D) band at 600 cm
-1 for the as-synthesized catalyst than the reported standard. Furthermore, the information regarding the site occupancy of the active site (Ni) in these catalysts was obtained by calculating the change in FWHM of the F
2 band. To further correlate the concentration of oxygen vacancies to the position of the active site (Ni) in the lattice, surface sensitive electronic characterizations such as X-ray photoelectron (XPS) and soft X-ray absorption spectroscopy (XAS) were performed. The oxidation state of Ni was identified as 2+, indicating that the metallic Ni clusters are not present. Furthermore, the local bond structure and geometry of the active site was accurately probed from Ni L2,3 edge XAS measurements in addition to the site occupancy measurements from Raman spectroscopy. These preliminary results on CZO-Ni catalysts demonstrate that controlling the oxygen vacancies in the lattice by varying the position of the active site (Ni) is the first step to understand the diffusion of the active site during a reaction and deactivation pattern of the catalyst.
Quantum-Espresso is an open-source software widely used for predicting the properties of materials from first principles [P. Giannozzi et al., Journal of Physics: Condensed Matter 21, 395502 (2009)].

In this tutorial, we will train the participants on how to use the Quantum-Espresso software for different applications. The focus is on the simulation of molecular species, metal electrodes, and semiconductor photoelectrodes under electrochemical conditions using the self-consistent continuum solvation (SCCS) model [O. Andreussi, I. Dabo, N. Marzari, Journal of Chemical Physics 136, 064102 (2012)].

URL: www.quantum-espresso.org; www.quantum-environment.org

The tutorial will follow the format adopted in previous Quantum-Espresso workshops. It will contain brief overviews of the theory being the codes, followed by tutorials and hands-on activities. The morning session will cover: Fundamentals of Density-Functional Theory and the afternoon session will cover: Quantum Chemistry in Continuum Environments.

8:30 AM
Overview of Density-Functional Theory Ismaila Dabo; The Pennsylvania State University

The first lecture will cover the basic concepts behind DFT simulations using a plane-waves basis set and pseudo-potentials to treat core electrons. The main flavors of DFT, their advantages and their limitations for the study of molecular species, bulk metals and semiconductors, interfaces and heterogenous systems will be reviewed.

9:45 AM BREAK

10:15 AM
Hands-ON: Equilibrium Structure Calculations Ismaila Dabo; The Pennsylvania State University

The core functionalities of the PWscf code of the open-source Quantum-ESPRESSO package will be explored: self-consistent electronic structure calculations, geometry and cell optimizations, simple ab-initio molecular dynamics simulations will be performed. An overview of input and output files and post-processing of the simulation results will be provided.

1:30 PM
Overview of Implicit Solvation Oliviero Andreussi; University of North Texas

Continuum embedding models in condensed-matter simulations will be reviewed, focusing on the recently developed self-consistent continuum solvation (SCCS) and to the soft-sphere continuum solvation (SSCS) models. Models to treat metal and semiconductor electrified interfaces will be reviewed.

2:45 PM BREAK

3:15 PM
Hands-On: Quantum-Continuum Solvation Oliviero Andreussi; University of North Texas

The core features of the Environ plugin to the PWscf code will be explored, including SCCS and SSCS simulations with default and non-default parameters. A comprehensive overview of input and output files, as well as post-processing and visualization of the simulation results, will be presented. Simulations of electrified interfaces and advanced continuum interfaces will also be included.
Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries and capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. In particular, I will discuss our progress to probe the solid/liquid interface across a range of metal/aqueous systems and the role halide ions play on the stability of the interfacial properties. Additionally, I will highlight some of our recent investigations into CO₂ adsorption phenomena on various metals as we move closer to developing the capabilities for studying CO₂ reduction under electrochemical conditions. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

11:00 AM ES06.01.02
Stimulated Raman Spectroscopy of Amorphous Oxide Catalyst During Oxygen Evolution Reaction
Chuhyon J. Eom and Jin Sunivich; Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

Understanding of the in-reaction structure and the functionality of a catalyst are closely connected. Detailed structural information can be revealed through vibrational techniques; however, a number of challenges need to be overcome. For instance, low scattering rates for Raman spectroscopy have made in-situ Raman of catalysis difficult. In this contribution, we demonstrate stimulated Raman spectroscopy (SRS) as an in-situ probe to address the challenge of low scattering rates in Raman. As a nonlinear spectroscopic technique, SRS holds several advantages including efficiency. Leveraging the improved efficiency, we apply SRS to measure the vibrational structure of an amorphous cobalt oxide catalyst during the oxygen evolution reaction (OER). Additional experiments using isotope labelling are used to identify the nature of the vibration structure. These results present the potential of SRS as a useful tool to investigate the much sought-after catalyst surface in-situ. The spectroscopic techniques, methods of analysis, and the experimental results will be presented.

11:15 AM ES06.01.03
Introducing Geometric Distortions in Disordered Nickel (Oxy)hydroxide Electrocatalysts by Incorporation of Fe(III)  Rodney Smith and Holger Dau; 1University of Waterloo, Waterloo, Ontario, Canada; 2FB Physik, Freie Universität Berlin, Berlin, Germany.

The dramatic change in electrochemical behavior of nickel (oxy)hydroxide films upon incorporation of Fe ions provides an opportunity to establish effective electrocatalyst design principles. It is well established that the addition of miniscule amounts of Fe(III) ions to nickel (oxy)hydroxide results in significant improvements in kinetics for the electrocatalytic water oxidation, but the chemical understanding of these gains remains a matter of debate. This presentation will introduce and discuss an asymmetric geometric distortion that was revealed by structure-property analysis of a series of disordered Fe–Ni (oxy)hydroxides. [1] These distortions were revealed by first identifying prominent structural motifs in the composition series by X-ray absorption spectroscopy, then correlating their structural descriptors to electrochemical and structural data acquired by in-situ UV-visible spectroelectrochemical data. Structural analysis indicated the presence of di-µ-hydroxo Ni-Ni and di-µ-hydroxo Ni-Fe motifs, with relatively important resonances on Fe-content. Both motifs exhibit trigonal distortions away from ideal octahedral coordination environments, imparting a local D₃₄ symmetry that is known in crystalline β-Ni(OH)₂. The distortion of Ni-Ni motifs in both the oxidized and reduced phases of the disordered materials is comparable to that observed in β-Ni(OH)₂, with O-Ni-O bond angles of 82°. The Ni-Fe motif contrasts with this, exhibiting a relaxed distortion in the reduced phase (84°-degree bond angle) and an increased distortion (<80-degree bond angle) in the oxidized phase. Spectroelectrochemical experiments reveal a previously unreported change in optical absorbance at ca. 1.5 V vs. RHE in Fe-containing samples, which is assigned as the oxidation of Ni(II) ions in the distorted di-µ-hydroxo Ni-Fe motif. A mechanism is proposed wherein the pre-catalytic redox process is assigned to oxidation of Ni-Ni motifs, while the catalytic process is decoupled from this process and assigned to the electrochemical oxidation of Ni sites in the Ni-Fe motif. The asymmetric distortion is attributed to the redox-inactivity of the Fe(III) ions in the material and the favored Fe(II)-O bond length being located between that of Ni(II)-O and Ni(IV)-O.

systems. In specific, we have developed an on-chip electrical transport spectroscopy (ETS) approach for directly probing the electrochemical surfaces of metallic nanocatalysts under in operando conditions, using ultrathin PdNWs as model electrocatalysts. Our results show a high degree of consistency with generally accepted conclusions in platinum electrochemistry, and provide important new insights into various technologically important electrocatalytic (such as fuel cell) reactions. This study defines a novel nano-electronic on-chip characterization strategy, as an alternative to the traditional spectroscopic characterization techniques, for in situ electrochemical surface studies with high surface sensitivity and surface specificity. The on-chip nano-electronic investigations have been further applied to investigate the anisotropic surface adsorptions on platinum surface, in simulating their competitive adsorption behavior with oxygenated species and correlating them to the electrokinetics of the oxygen reduction reaction (ORR). The ETS enables highly sensitive characterization of anionic adsorption and opens an efficient pathway to address the practical poisoning issue (at trace level contaminations) from a fundamental perspective. Additionally, ETS has also been applied to reveal the charge transport mechanism and the electrochemical behavior in electronic microbes (including Shewanella and Geobacter, two widely used microbes in microbial fuel cells), which has been a subject of on-going debate. Our results elucidate the complex basis of electrical conductivity of both individual microbial cells and biofilms, and have led to a new model revealing the electrochemical origin of microbial conductivities.

1:30 PM *ES06.02.01
Catalyst Development for Water Electrolysis and Fuel Cell Reactions Involving H2, O2, H2O, and H2O2 Thomas Jaramillo1, 2; 1Chemical Engineering Dept., Stanford University, Stanford, California, United States; 2SUNCAT Center for Interface Science and Catalysis, Stanford University, Stanford, California, United States; 3Photon Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Water electrolyzers and fuel cells are promising technologies that can play a role in a sustainable future. Catalyst development is needed to advance these systems, to improve performance and to lower costs such that the systems can be cost-competitive with respect to conventional technology. This talk aims to describe catalyst development challenges and opportunities within this area. The focus will be on catalyzing interconversions involving H2, O2, H2O, and H2O2, with an emphasis on low- or zero-precious metal content catalyst materials. Examples will be given for catalyst design from first principles, the development of materials based on those principles, and their integration into functional devices.

2:00 PM *ES06.02.02
Molecular Understanding of the Oxide Electrocatalyst Surface Kelsey A. Stoerzinger1; 1Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States; 2School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, Oregon, United States.

Oxide catalysts are an important class of electrocatalysts for the oxygen reduction and evolution reactions in fuel cells and electrolyzers. Electrochemical studies of well-defined surfaces grown by pulsed laser deposition or molecular beam epitaxy establish the intrinsic activity of oxide catalysts in a way that cannot be realized with polydisperse nanoparticle systems, and can also reveal how different terminations1 and structures2 affect the energetics and kinetics. Furthermore, the surface speciation of epitaxial films in an aqueous environment can be quantitatively assessed in situ using ambient pressure X-ray photoelectron spectroscopy. Understanding oxide electronic structure in an aqueous environment is also critical for promoting charge transfer reactions. To this end, we investigate changes in the electronic structure as a function of the oxygen and water chemical potential, enabling comparison with the metal redox potential and catalytic activity.3 The resultant molecular-level understanding of interfacial interactions developed from epitaxial surfaces can guide the rational design of high-surface-area oxide catalysts for technical applications.

References

2:30 PM ES06.02.03
Combining Electrochemistry, Surface Science and Density Functional Theory to Identify Electrocatalytic Structure-Property Relationships in OER Catalysts Douglas R. Kaufman1, Xingyi Deng1, 1National Energy Technology Lab, Pittsburgh, Pennsylvania, United States; 2AECOM, South Park, Pennsylvania, United States.

We present an approach that couples electrochemistry, surface science, and density functional theory (DFT) calculations to precisely identify structure-property relationships in electrocatalytic oxygen evolution reaction (OER) catalysts. The OER is an essential component in electrochemical CO2 conversion systems, and mixtures of nickel, cobalt, and iron have shown remarkable alkaline OER activity that exceeds state-of-the-art IrOx. However, atomic-level understanding of how OER activity evolves with the catalyst shape, size, composition, and support are still lacking in the literature. Our approach grows well-defined transition metal electrocatalysts with precisely controlled morphology, composition, and loading. Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy quantify the catalyst loading (mol/cm2), number density (particles/cm2), and morphology with unrivaled spatial resolution. Electrochemical testing then correlates mass activity, turnover frequency, and specific current density with the catalyst structure and composition. We find clear experimental and computational evidence for edge-enhanced OER at pure FeOx structures, and this insight was translated into the synthesis of a nanoparticulate analog for demonstration in alkaline electrolyzer devices. On the other hand, mixed metal NiFe systems showed a more complex evolution of structure-dependent activity that did not directly depend on the relative density of under-coordinated edge sites. Our approach provides atomic-level structure-property relationships for emerging OER catalysts that can be used to guide scalable synthetic strategies and expedite the deployment of more energy efficient electrocatalyst systems.

2:45 PM ES06.02.04
Measurements of Oxygen Electroadsorption Kinetics on RuO2(110) and IrO2(110) Ding-Yuan Kuo, Hanjong Paik, Jocienne Nelson, Kyle Shen, Darrell Schlom and Jin Suntivich; Cornell University, Ithaca, New York, United States.

RuO2 and IrO2 are among the best catalysts for the oxygen evolution reaction (OER), an electrochemical reaction that limits the efficiency of water splitting. The high activity of these rutile oxides has been attributed to their ability to stabilize the OER intermediates via electroadsorption which involves related elementary proton and electron transfer steps related to the oxygen electroadsorption are still unclear. In this presentation, we present our measurements of these kinetics on well-defined RuO2 and IrO2 surfaces. We use rate-dependent cyclic voltamnograms to extract the rates of the oxygen electroadsorption on RuO2 and IrO2. Well-defined surfaces are used to minimize convolution from different facets. We further identify the pathway and related fundamental rate laws by investigating the influence of different electrolytes on kinetics. Our results provide insights into the kinetics of oxygen electroadsorption on oxides and the fundamental origin of the sluggishness in the OER kinetics.

3:00 PM BREAK

3:30 PM *ES06.02.05
Identify Atomic-to-Nano Structures and Structure Evolution of Pt and PGM-Free Electrocatalysts for Oxygen Reduction Reaction Vivyan Shao; Pacific Northwest
Oxygen reduction reaction (ORR) catalysts account for the largest efficiency loss and one of the largest cost portions of PEM fuel cells. There has been intensive research effort on ORR electrocatalysts from precious metals to nonprecious metals (also called platinum group metal (PGM)-free catalysists). Developing highly efficient precious metal electrocatalysts and highly active PGM-free catalysts remains a grand challenge, and finding catalysts that are stable and durable in the harsh PEM fuel cell environment is even more challenging. In this talk, we will discuss our research to understand the instability of the catalysts from materials innovation to advanced characterization. We will introduce our environmental TEM study of PGM catalysts, PGM-free catalysts instability and the proposed solutions.

4:00 PM ES06.02.08
Modification of Fuel Cell ORR Catalyst Surface with Organic Ligands for Enhanced Activity and Durability—The Effect of Ligand Structures Yuta Ikehara, Tomoyuki Nagari and Hironori Hiai; 1Fuel Cell System & Component Design Department, Toyota Motor Corporation, Toyota, Japan; 2Materials Research Department, Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

Recent advances of polymer electrolyte membrane fuel cell (PEMFC) technology has been substantial and successfully led to the commercialization of fuel cell electric vehicles (FCEVs) such as Toyota Mirai. However, the continuation of FCEV development is facing several hurdles, of which one major issue is related to the high cost of fuel cell system as compared to conventional engines. Economic analysis has shown that catalysts is by far the most expensive material component for high production volume. [1] Current state-of-art PEMFCs use platinum-based catalysts to speed up hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) on the anode and the cathode, respectively. While the HOR proceeds very fast on Pt surface, the ORR has a sluggish kinetics, as it involves sequential steps of proton coupled electron transfer processes and a “scaling” issue makes it difficult to optimize every elemental reaction step simultaneously. [2]

Many previous works have focused mainly on ORR catalyst material properties, for example, alloy, core-shell, shape control and so on. Engineering catalyst-electrolyte interface properties may offer another way to overcome the problem. One recent effort involves the modification of Pt catalyst surface with organic ligands and has demonstrated some successes in enhancing catalyst activity. [3-5] The improvement was mostly attributed to either the change of surface structural material of the catalyst, or the protection of Pt active sites from poisoning by strong anion adsorption. [6-8] In this study, we systematically examined a series of organic ligands with different structures. Combining material characterization with electrochemical analyses allowed us to assess not only the catalyst activity and durability, but also the ligand stability. Such a comparative study is expected to provide additional insights on ligand structural design for further improvement of catalyst performance.

References
(7) M. Kobayashi, et al., ECS Abstract MA2018-01 2360

4:15 PM ES06.02.07
Optimization of Pt Loading Ratio in Low Pt-Cathode Catalysts for PEFC Application Kenta Inaba 1, Toshihiko Manda 1, Tatsuya Takeguchi 1, Yasuo Kaneda 2 and Koichi Urui 1; 1Faculty of Science and Engineering, Iwate University, Morioka, Japan; 2JUKES Inc., Kui, Japan.

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as one of the highly efficient power sources for fuel cell vehicles. A large amount of platinum (Pt) is used in general as electrode catalysts to improve reaction kinetics – an oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) on the cathode and anode sides, respectively. Pt loading ratio on the electrode is critical. In PEFC, the Pt loading ratio on the electrodes is considered as a practical use of large-scale PEFCs. In this study, we studied the effect of the Pt loading ratio and carbon supports (C) on ORR activity of the Pt/C cathode catalysts. Well-dispersed Pt nanoparticles were successfully loaded on the two carbon supports having different surface area and pore distributions. The ORR activity of the resulting Pt/C catalysts was evaluated with respect to the mass activity, electrochemically active surface area (ECSA), and cell voltage under PEFC operation.

Two Ketjen black (ECP300J and ECP600JD, LION) were used as a carbon support. The Pt/C catalysts with different Pt loading ratio, Pt/C = 20 - 40 %, were prepared by the ethanol reduction method. The specific surface area and pore size distribution of the carbon support with and without Pt loading were determined by Brunauer-Emmett Teller (BET) measurements. The mass activity and ECSA of a series of Pt/C catalysts were evaluated by the Koutecky-Levich plot at 0.7 V vs. RHE and CO stripping, respectively, by using the rotating disk electrodes. The fuel cell tests were carried out by using the membrane electrode assembly (MEA) consisting of the prepared Pt/C cathode catalysts, commercial Pt/C anode catalysts, and typical polymer electrolyte membrane (Nafion). The Pt loading in the cathode and anode was fixed at 0.1 and 0.5 mg-cm⁻², respectively. The I-V polarization curves were measured at 70 °C with the steady flow of fully humidified O₂ and H₂ gases into the cathode and anode, respectively. In the prepared Pt/C catalysts, the Pt particles were well dispersed on the carbon supports with the average diameter of 1.8 nm, almost irrespective of the Pt loading ratio. The mass activity and ECSA however indicate the presence of superior number of active sites for the catalysts using ECP600JD as a support. The BET analysis on the Pt/C catalysts also supports the larger specific surface area of the Pt/C catalyst with ECP600JD than that with ECP300J. Intrinsically large surface area of the ECP600JDs a likely reason. The ORR activities of the MEAs clearly reflects the mass activity and ECSA of the Pt/C cathode catalysts. The MEAs with Pt/C catalysts with ECP600JD indeed showed higher cell voltage than those with ECP300J at the same current density. On the other hand, the ORR activity of the Pt/C catalysts was not proportional to the Pt loading ratio, but local maxima were observed at around 35%. As the Pt loading ratio was fixed, the thickness of the catalyst layer decreases thicker with increasing the Pt loading ratio, while mass activity decreases. A balance between the thickness of the catalyst layer and the number of active sites would predominant the ORR activity of the Pt/C cathodes under PEFC operation.

4:30 PM ES06.02.08
Catalytic Activity of Oxygen Reduction Reaction on Mono-Layer Molecule Electrode using the Transition-Metal Oxide Nanosheet Takahiro Saida, Miyu Mashiyma and Takahiro Maruyama; Meijo Univ., Nagoya, Japan.

Polymer Electrolyte Fuel cell (PEFC) is attracted attention as one of the next generation power sources because it exhausts theoretically only water. However, its high cost and short service life are inhibiting the wide-spread commercialization. It is thought as one reason that this is attributing to using the platinum-based electrocatalyst. To reduce cost and lengthen service life radically, the non-platinum-based catalyst such as oxide, carbon-allowing and the enzyme has been developing. The oxide-based catalyst has the high possibility as the alternative the platinum-based catalyst due to possessing the high stability under PEFC operation conditions. Several researchers had reported that a part of oxide, such as group 4- and 5-metal oxide and precious metal oxide, showed the high activity of oxygen reduction reaction (ORR). However, these ORR activity does not achieve that of the conventional platinum catalyst. One reason for this situation is the active site on oxide surface is not fully understanding as the common recognition. Thus, it is hard to advance the new concept to increase the active site density. The situation inside the catalyst layer during the ORR progress is too much complex since it needs to take consideration with the diffusion of oxygen, proton, electron, and water in catalyst layer other than the ORR mechanism on the oxide surface.

Therefore, we focused on the mono-layer molecule electrode forming by the metal oxide nanosheet in order to exclude a variety of the diffusion resistance on an electrode. This study focused on the role of the oxygen vacancy site on titanium oxide nanosheet (TiO₂ns) and titanium-niobium oxide nanosheet (TiNbO₂ns) and the redox site on nuthenium oxide nanosheet (RuO₂ns) for the ORR.

A mono-layer molecule electrode was prepared by Layer by Layer method combining with the poly-cation copolymer and each transition-metal oxide nanosheet. Various types of transition-metal oxide nanosheets were synthesized along previous literature. The deposition condition of transition-metal oxide nanosheet on the substrate was observed by AFM. The electrochemical measurement was conducted by the rotating disc electrode as the reference and a carbon rod as the counter electrode. At that time, 0.1 M HClO₄ at room temperature was employed as the electrolyte. ORR activity was evaluated by the potential at -0.05 mA cm⁻² of difference current between oxygen flow conditions and nitrogen flow conditions.

The ORR activity of RuO₂ns mono-layer electrode showed about 0.6 V which was almost agreed with that of evaluation used powder sample. Addition, the redox peaks of RuO₂ns were clearly observed also in a mono-layer electrode. Thus, it is thought that a mono-layer electrode, which was prepared by Layer by Layer method, was also possible to evaluate accurately the electrochemical behavior including of ORR activity. In the case of TiNbO₂ns without oxygen vacancy or Nb doping, the ORR activity was lower than that of RuO₂ns.
Thus, it is thought that ORR activity depends on the kind of transition metal.

4:45 PM ES06.02.09
Maximization of Quadruple Phase Boundary for Alkaline Membrane Fuel Cell Using Non- Stoichiometric α-MoO3 as Cathode Catalyst Xuan Shi1, AM Kamann1 and Haotao Zheng2; 1Arizona State University, Mesa, Arizona, United States; 2MSM, Council for Scientific and Industrial Research, Pretoria, South Africa.

Oxygen can only be reduced at the quadruple phase boundary (catalyst, carbon support, ionomer and oxygen) of the cathode catalyst layer with the non-conducting electrocatalyst. To maximize the quadruple phase boundary sites is crucial to increase the peak power density of each membrane electrode assembly. The quadruple phase boundary is depending on the ratio of catalyst, carbon support and ionomer. The loading of the catalyst layer is also crucial to the fuel cell performance. In this study, the non-stoichiometric α-MoO3 manganese dioxide nanorod material has been synthesized and the ratios of carbon, ionomer, and catalyst loadings were optimized in alkaline membrane fuel cell. In total, ten membrane electrode assemblies have been manufactured and tested. Taguchi design method has been applied in order to understand the effect of each parameter. The conclusion finds out the ionomer has more influence (68% factor effect) on the alkaline fuel cell peak power performance than carbon and loading.

SESSION ES06.03: High-Temperature Electrochemical Analysis
Session Chairs: Kelsey Stoezinger and Jim Suntivich
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 122 C

8:45 AM ES06.03.01
In Situ/Operando XRD Study of a Reversible PtOx Formation at the Pt/YSZ Interface Sergey A. Volkov1, Alexander Hutterer2, Pirmin Lakner1, Florian Bertram1 and Vedran Vonk1; 1DESY, Hamburg, Germany; 2Technische Universität Wien, Vienna, Austria.

Complexity of the fuel cell technology drives researchers to study different model systems in order to get insight into the processes during Solid Oxide Fuel Cell (SOFC) operation. One of such model systems is a Pt/YSZ where platinum plays role of a cathode on yttria-stabilized zirconia (YSZ) electrolyte. Different phenomena may lead to undesirable electrode deactivation. Along with irreversible morphological changes (e.g. film dewetting, blistering), another process, observed as an additional resistivity during anodic polarization, hinders oxygen transport in our model-electrode system. This process is assigned to the formation of Pt “phase” oxide at the Pt/YSZ interface and triple-phase boundaries. PtOx is predicted to be responsible for passivation of the working electrode in Pt/YSZ model systems. Indirect but convincing evidences of electrochemically driven Pt oxidation on well-defined Pt electrodes are present in several studies. Although there is still a debate on the exact mechanism of PtOx formation and its structure (PtO, PtO2 or Pt2O3), there is no doubt it influences oxygen exchange kinetics, which decreases electrocatalytic activity of an electrode in Pt/YSZ model system. Employing X-ray diffraction (XRD) combined with electrochemistry measurements at beamline P08, Petra III Synchrotron, DESY, Hamburg, we provide first direct evidence of the existence of PtOx phase at the Pt(111)/YSZ(111) interface after anodic polarization, which decomposes once the potential is reversed. In situ/operando surface XRD on electrode/electrolyte interface reveals its structure and evolution on atomic scale. Our results show feasibility of applying synchrotron based surface XRD to study fuel cell related electrode/electrolyte model interfaces operando and contribute to better understanding of a complex multistep oxygen reduction and evolution reactions in electrochemical devices, such as SOFCs and oxygen lambda sensors.

9:00 AM (+)ES06.03.03
Thermochemical and Electrochemical Trends in the Ceria-Zirconia System Sossina M. Haile1 Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States.

Introduction of zirconia into ceria is known to enhance the reducibility of the latter, despite the fixed tetravalent state of zirconium. Here we use a host of techniques to explore the origin of this behavior, its relevance to surface oxidation state, and its impact on kinetic properties. We find, for example, from in situ XANES (X-ray Absorption Near Edge Spectroscopy) that while the surface of ceria is reduced relative to the bulk whether or not zirconium is present, the extent to which the surface and bulk regions differ depends strongly on the Zr concentration. Specifically, with increasing Zr, the differential between the two regions diminishes. In parallel, using electrical conductivity relaxation methods, it is observed that the bulk chemical diffusion of oxygen in Ce0.8Zr0.2O2−δ is lower than that in undoped ceria. The connections between these and related observations is discussed.

9:30 AM ES06.03.04
Nanoscale Design of Grain Boundary Composition for Improved Ionic Conductivity in CeO2 Ceramics Tara M. Boland1, Peter Rez2 and Peter Crozier2; 1Materials Science and Engineering, Arizona State University, Tempe, Arizona, United States; 2Physics, Arizona State University, Tempe, Arizona, United States.

Ceramic oxides are used for a wide variety of technologically relevant applications from electrochemical devices, novel resistive switching devices and oxygen sensors. Applications such as these typically rely upon the ability of oxides to conduct ions efficiently through the lattice. For oxides, such as CeO2 (ceria), it is common to dope with alternative elements to increase the number of available charge carriers. While the methods developed for bulk-doping have been successful, they have provided little insight when optimizing the grain boundary (GB) ionic conductivity in polycrystalline ceramic oxides. Recent nanoscale compositional characterization has shown different nominal concentrations could result in orders of magnitude increase in GB ionic conductivity relative to the undoped samples [1]. This effect has been attributed to increases in local dopant/solute concentrations at the GB. This study aims to predict the optimal dopants that, when present in high concentrations, increase the ionic conductivity across the GB.

To show how the various dopants modulate the ionic conductivity across the GB, computational modeling is employed using molecular statics to optimize the GB interfacial structure for three symmetric tilt and one twist GB in CeO2. The GB structures are then doped using a high concentration profile obtained from ref 1. Molecular dynamics simulations are performed to correlate migration energetics with changes in conductivity for the various dopants. The energetic and structural properties of various oxygen migration pathways are compared for each dopant species to ascertain how nanoscale composition and local atomic structure can modulate ionic conductivity across GBs. The trends obtained using molecular dynamics are validated using density functional theory calculations. This study further develops our understanding of high solute GB composition and structure, enabling the development of methods such as selective doping to improve macroscopic ionic conductivity for both the grain and GB.

[2] We gratefully acknowledge ASU’s HPC staff for support and assistance with computing resources, NSF grant DMR-1308085, and ASU’s John M. Cowley Center for High Resolution Electron Microscopy.

9:45 AM ES06.03.06
Determining the Atomic Structures at Fluorite-Perovskite Interfaces Bonan Zhu1, Georg Schusterlighthouse1, Ping Lu1, Judith L. MacManus-Driscoll2 and Chris J. Pickard1; 1Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 2Advanced Institute for Materials Research, Tohoku University, Sendai, Japan; 3Sandia National Laboratories, Albuquerque, New Mexico, United States.

Interfaces play important roles in many functional thin film devices. However, the atomic configurations at interfaces between two phases with different crystal structures are not easily determined experimentally, yet they are the key for understanding the properties induced. Vertically aligned nanocomposites (VAN) typically have pillar-matrix nanostructures combining two distinct phases. Up to two orders of magnitude increase in out-of-plane ionic conductivity was observed using Sm-doped CeO2 (SDC)/SrTiO3 (STO) VAN films grown on STO substrates. To investigate the roles of vertical interfaces, we used random structure searching to explore the atomic configurations at the vertical interfaces. The structures were found to contain any features that promoted interfacial oxygen diffusion. Instead, they suggested that vacancy movement may be suppressed near the interface due to the existence of trapping sites. In addition, motivated by the controversies claims of enhanced ionic conductivity at yttria stabilized zirconia (YSZ)/STO planar interfaces,
we performed fully first-principles random structure searching at a model CeO$_2$/STO (001) interface. We found previously unknown stable interfaces structures that differ from the bulk phases. Vacancy formation energies and diffusion pathways were studied and their effects on ionic conductivity will be discussed.

10:00 AM BREAK

10:30 AM *ES06.03.05
Strategic Design of Catalysts and Electrolytes for the Electrochemical Reduction of CO$_2$: Alexis Bell, University of California, Berkeley, Berkeley, California, United States.

Recent experimental studies have shown that the electrochemical reduction of CO$_2$ depends on many factors, including the composition and structure of the electrocatalyst, the composition of the electrolyte, and the effects of mass transfer between the bulk electrolyte and the catalyst. The choice of electrocatalyst affects the principal products produced. For example Ag would be the catalyst of choice to reduce CO$_2$ to CO, whereas Cu would be the preferred catalyst for the production of C$_2$H$_4$ hydrocarbons and alcohols. The choice of alkali metal cation used for the electrolyte also influences catalyst activity and product selectivity. For both Ag and Cu, the action and the selectivity towards forming carbon-containing products versus hydrogen is strongly enhanced by using Cs$^+$ rather than Li$^+$. Mass transfer of from the electrolyte to the catalyst and of OH$^-$ anions from the catalyst to the bulk electrolyte also affect the product distribution. It will be shown that manner in which mass transfer affects the distribution of product formed during the electrochemical reduction of CO$_2$ is best understood from simulations of a complete electrochemical cell. This point will be illustrated based upon simulations of CO$_2$ reduction occurring in an aqueous electrolyte containing planar electrodes.

11:00 AM ES06.03.07
CO Site Preference on Copper Surfaces in Electrochemical Environments—Deciphering Voltage and Electrolyte Composition Effects: Stephen E. Weitzner, Sneha A. Akhade, Joel B. Varley, Brandon C. Wood, Sarah E. Baker and Eric B. Duoss; Lawrence Livermore National Laboratory, Livermore, California, United States.

The development of effective electrocatalysts to convert carbon dioxide into value-added products such as methane and ethylene requires a detailed atomistic understanding of the reaction pathway. While it is well known that copper (100) surfaces exhibit a higher selectivity towards ethylene production, both electrochemical and non-electrochemical pathways have been proposed to describe this process. In both cases, the presence of adsorbed CO plays a crucial role and the pathways are observed to be active under different conditions. In this work, we study the role of the electrochemical environment in stabilizing CO across different copper surface sites and evaluate the energy barriers of key steps in the carbon dioxide electroreduction pathway. Using the recently developed Effective Screening Medium—Reference Interaction Site Method (ESM-RISM), we provide a detailed assessment of the roles of both applied voltages and electrolyte composition effects. Our results demonstrate that these two factors are synergistic, leading to behavior that qualitatively deviates from conventional models.

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

11:15 AM ES06.03.08
Hierarchical Quasi-1D CuO$_x$-Derived Nanostructured Copper Catalysts for CO$_2$ Reduction: Giorgio Giuffredi$^{1,2}$ and Fabio Di Fonzo$^1$; Istituto Italiano di Tecnologia, Milano, Italy; $^2$Department of Energy, Politecnico di Milano, Milano, Italy.

Electrochemical reduction of emitted CO$_2$ to fuels and complex hydrocarbons represents a promising solution to efficiently store intermittent, renewable energies-generated electricity in the form of chemical energy of carbon-based fuels. Copper is one of the most interesting CO$_2$ reduction electrocatalysts, thanks to its ability to reduce carbon dioxide to complex hydrocarbons with good efficiency, however when in bulk polycrystalline form it has low activity and requires a high overpotential for the reduction reaction. Oxide-derived Cu catalysts are one of the most efficient way to increase the intrinsic activity of Cu: this class of materials have higher selectivity for complex hydrocarbons and longer stability. Moreover, their CO$_2$ reduction activity and selectivity are strongly affected by the morphology, which controls the mass transport of the reactants to the active sites and influences the local pH. In this contribution, the CO$_2$ reduction activity and selectivity of Cu catalysts derived from the reduction of Copper Oxide (CuO$_x$) hierarchical nanostructures with different structural features are investigated.

We propose an approach that couples two aspects: the first one is employing an amorphous CuO$_x$ material, which presents a higher availability of undercoordinated surface sites which, coupled with the high surface area, increases the activity. The second aspect is controlling the morphology of the CuO$_x$ nanostructures down to the nanoscale by exploiting Pulsed Laser Deposition (PLD) as synthesis method: this technique, in fact, allows for a fine control over the deposit morphology by finely tuning the deposition parameters. In this way, the chemical composition and thickness of the hierarchical quasi-1D nanostructures are kept constant and it is possible to modify their aspect ratios, their nanostructuring and their micro- and nanoparticles diameters. With this approach, it is possible to evaluate the effect of the nanoscale morphological features on the overall catalytic activity – that is, on a smaller length scale than what is usually performed for Oxide-derived Copper catalysts.

Characterization of the PLD-synthesized nanostructures shows an amorphous matrix with embedded crystalline seeds of CuO and Cu$_2$O, differently from other reported oxide-derived Cu catalysts. CO$_2$ reduction performance of the oxide-derived Cu nanostructures is assessed through chromatographic measurements in aqueous electrolyte, showing good current densities up to -60 mA cm$^{-2}$ and a good stability for at least one hour of prolonged operation. Liquid products analysis, performed via $^1$H NMR spectroscopy, shows a high productivity of ethanol at limited potentials applied (V=-0.4 V RHE).

This contribution shows how coupling an amorphous, oxide-derived Cu catalyst with a fine control over morphology can be an efficient way to increase the activity of CO$_2$ reduction catalysts.

11:30 AM *ES06.03.09
Isolated Transition Metal Single Atom Catalysts for Selective CO2 Reduction: Haotian Wang; Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States.

The development of highly selective and earth-abundant electrocatalysts for CO$_2$ reduction is becoming increasingly important for renewable energy applications. The challenge here is the strong competition from water reduction, as well as the low selectivity towards a desired product. In this talk I will introduce the rational tuning of electronic properties of catalytic materials for their significantly improved CO$_2$ reduction performance. By dispersing transition metals into isolated single atoms with electronic structures significantly different from their bulk counterparts, we can dramatically suppress the competing hydrogen evolution and deliver an ultra-high CO$_2$ reduction selectivity of more than 95% under ambient conditions in water.

1:30 PM *ES06.04.01
Enhanced Electrocatalytic Activities of Ruddlesden-Popper Catalysts for the Oxidation of Urea and Small Alcohols By Active Site Variation: Keith Stevenson$^2$ and Robin Forslund$^1$; $^1$University of Texas at Austin, Austin, Texas, United States; $^2$Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

The electrooxidation of urea continues to attract considerable interest as an alternative to the oxygen evolution reaction (OER) as the anodic reaction in the electrochemical generation of hydrogen due to the lower potential required to drive the reaction and the abundance of urea available in waste streams. Herein we investigate the effect of Sr
substitution in a series of LaxSr1-xNiO4+δ Ruddlesden-Popper catalysts on the electrooxidations of urea, methanol, and ethanol and conclude that activities toward the urea oxidation reaction increase with increasing Ni oxidation state. The 75% Sr-substituted LaxSr1-xNiO4+δ catalyst exhibits an exceptionally high mass activity of 588 mA and 7.85 A for the electrooxidation of urea in 1 M KOH containing 0.33 M urea, demonstrating the potential applications of Ni-based Ruddlesden-Popper materials for direct urea fuel cells and low-cost hydrogen production. Additionally, we find the same correlations between Ni oxidation state and activities for the electrooxidations of methanol and ethanol, as well as identify processes that result in catalyst deactivation for all three oxidations. Most importantly, this is the first demonstration of how systematically increasing Ni – O bond covalency by pushing the formal oxidation state of Ni above +3 serves to increase catalyst activity for these reactions and will act as a governing principle for the rational design of catalysts for the electrooxidation of urea and other small molecules going forward.

2:00 PM *ES06.04.02
Active Sites and Activity of Sub-/Multi-Atomic Layer Electrocatalysts on Tetrahexahedral Nanocrystals Shi-Gang Sun; Xiamen University, Xiamen, China.

Tetrahexahedral nanocrystals (THI NCs) of face-centered-cubic (fcc) metals such as Pt, Pd, Rh are enclosed with high-index facets and present a high density of step sites on their surfaces, and exhibit therefore a high electrocatalytic activity for oxidation of small organic molecules that serves as anode reaction in direct fuel cells. To further identify the active sites on THI NCs and investigate the activity of sub- and multi-atomic layer electrocatalysts on the THI NCs are significant in rational design and preparation of electrocatalysts with low-precious metal and superb property. The current study focuses on the identification of surface active sites on the THI Pt NCs through applying cyclic voltammetry (CV) and in situ FTIR spectroscopy and using CO adsorption and oxidation as probe reactions in order to understand their role in practical electrocatalysis, and demonstrates that the surface structure of nanocrystals with high-index facets can be tuned precisely and continuously by carefully adjusting the electrochemical conditions upon their synthesis. The finely-tuned nanocrystals could play as model electrocatalyst at nanoscale to gain the structure-catalytic functionality relationship under realistic application conditions. Furthermore, the electrocatalytic properties of small organic fuel molecule oxidation of sub-monolayer of adatoms as Bi, Ru and Au on THI Pt NCs and multi Pt atomic layer on THI Pt NCs were studied to reveal the structure effect and interaction of atoms/layers with nanocrystals of high-index facets in electrocatalysis.

Acknowledgement: This work was supported by Natural Science Foundation of China (21573183, 21621091).

References:

2:30 PM BREAK

SESSION ES06.05/ES05.06: Joint Session: Cooperative Catalysis
Session Chairs: Wonchao Sheng and Jin Suntivich
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 122 B

3:30 PM *ES06.05.01/ES05.05.01
Mechanisms and Selectivity of the Electrochemical CO2 Reduction Reaction on Multiple-Site vs Single-Site Catalysts Peter Strasser; Chemical Engineering, Technical University Berlin, Berlin, Germany.

Strategies for closing the anthropogenic carbon cycle using the chemical conversion of CO2 into useful molecules have become a scientific and technological priority. All chemical ways to convert CO2 into CO, oxygenates or hydrocarbons, the direct electrochemical coupling of water electrolysis and CO2 reduction appears attractive, as it is a one-pot process step, occurs at ambient temperature and pressures, involves solely water and CO2 as reactants, and may involve renewable electricity from wind, solar or hydro power plants.

The CO2 electroreduction is by and large carried out on the surface of metal catalysts. At industrially relevant current densities and electrode potentials, however, these catalysts typically suffer from low faradic CΟ2 product selectivities due to the competing, very fast reduction of water, i.e. the hydrogen evolution reaction. New catalyst concepts with tunable selectivity for hydrogen evolution versus CO2 reduction are needed.

In this contribution, we share recent comparative experimental and computational mechanistic insight in the electroreduction of CO2 on metallic multi-site versus molecularly inspired metal ion-N modified high surface area carbon single-site catalysts. We provide new insight into CO selectivity trends and put particular emphasis on the competing reaction pathways to methane and methanol. We show that carbon-based single site catalysts are an intriguing cost-effective alternative to their metallic rivals at industrial current densities.

4:00 PM *ES06.05.02/ES05.05.02
CO Oxidation on Supported Ir Single Atoms—Consequences of Strong CO Adsorption on Kinetics and Resting State of the Catalyst Ayman M. Karim; Virginia Tech, Blacksburg, Virginia, United States.

Supported single-atom catalysts provide an ideal system to study reaction mechanisms on a molecular level and to bridge heterogeneous and homogeneous catalysis. Single atoms have shown remarkably different activity and selectivity for several reactions, however for low temperature CO oxidation the reaction mechanism is not well understood and there is debate whether single atoms have higher intrinsic activity than nanoparticles. In this talk, the mechanism of CO oxidation on atomically dispersed Ir/MgAl2O4 catalysts will be presented and compared to that on nanoparticles. Using in-situ and in-operando DRIFTS and HERFD-XANES complemented by DFT calculations, we identified the active Ir single-atom complex, and resting state of the catalyst for low temperature CO oxidation. We provide evidence that strong CO adsorption on single atoms leads to an Eley-Rideal mechanism where Ir(CO) is the active complex (i.e. a CO ligand is present during the catalytic cycle). The results show that due to the ability of single atoms to coordinate with more than one ligand, strong adsorption by CO does not necessarily lead to catalyst poisoning. Additionally, we demonstrate that the unusual kinetics on single atoms can be used as a facile surface sensitive characterization tool for quantifying the number of single atom sites in catalysts containing a mixture of single atoms and nanoparticles. The results provide a new perspective for understanding reaction mechanisms and interpreting spectroscopic and catalytic activity of supported metal single atoms.

4:30 PM ES06.05.03/ES05.05.03
Oxide Bilayers as High Efficiency Water Oxidation Catalysts Through Electronically Coupled Phase Boundaries Jennifer Leduc; Sanjay Mathur and Thomas Fischer; University of Cologne, Cologne, Germany.
New semiconductor metal oxides capable of driving water-splitting reactions by solar irradiation alone are required for sustainable hydrogen production. Whereas most metal oxides only marginally deliver the photochemical energy to split water molecules, uranium oxides are efficient photoelectrocatalysts due to their absorption properties ($E_g = 2.0 - 2.6$ eV) and easy valence switching among uranium centers that additionally augment the photocatalytic efficiency. Although considered a scarce resource, the abundance of uranium compounds in the environment is manifested in the huge quantities of stored $Uf$ gas, produced as waste streams in the nuclear fuel enrichment process. Here we demonstrate that thin films of depleted uranium oxide ($UO_x$) and their bilayers with hematite ($a-Fe_2O_3$) are high activity water oxidation catalysts due to electronically coupled phase boundaries. The electronic structure of uranium oxides showed an optimal band edge alignment in $UO_x/Fe_2O_3$ bilayers (DFT calculations) resulting in improved charge transfer at the heterojunction as supported by TAS and XAS measurements. The enhanced photocurrent density of the heterostructures with respect to well-known hematite offers unexplored potential of uranium oxide in artificial photosynthesis.

4:45 PM ES05.05.04/ES05.05.04
Design of Supported Transition Metal Catalysts for Methane Partial Oxidation
Darinka Princic1,2, Julie Fornaciari1,2, Adam Weber2 and Alexis T. Bell1,2; 1Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The abundance of methane and its low cost makes it an optimal raw material for chemical precursors and energy-dense fuels. Conventional synthesis of methanol involves a multistep process, which requires high energy input and high cost [1]. Alternatively, electrochemical methane oxidation using a catalyst is a promising single-step approach to achieve a direct conversion of methane to methanol at lower temperatures and cost [2].

An efficient catalyst needs to be developed for this energetically challenging process. The catalyst should be active for C-H bond activation, thereby enabling oxidative hydroxylation of methane, and simultaneously inhibit further methanol oxidation. To date, a variety of the catalysts, including supported metals (Pd, Ru, Au, Ag) and metal oxides ($V_2O_5$, $Fe_2O_3$, $CoO$, $MnO_2$, $MoO_3$, $CrO_3$), have been tested in electrochemical cells and shown promise for this approach [2]. However, further systematic studies are essential for understanding the mechanism for methane oxidation and thereby enabling the rational design of the catalysts. In this regard, porous metal oxides and supported single-atom catalysts (SAC) are particularly interesting [3]. These catalysts show potential for high methane conversion and are ideal model catalysts to identify active sites and facilitate understanding of the reaction process at a molecular level. In spite of great interest; however, it still remains challenging to achieve atomically dispersed metals in high loadings for efficient catalysis.

In this study, a design of first-row transition metal oxides and MOF-derived supported single-atom catalysts will be presented. The catalysts are synthesized with wet-chemistry, and subsequently, characterized for electrochemical methane-to-methanol oxidation. Structural and chemical analyses of catalysts using a combination of various microscopic and spectroscopy techniques are used to establish structure/property relationship. These insights provide valuable basis for a scientific-guided approach toward new metal oxide and supported single-atom catalysts for this challenging process.


SESSION ES06.06: Electrocatalysis III
Session Chairs: Oliviero Andreussi and Wenchao Sheng
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 122 C

8:30 AM ES06.06.02
Three-Dimensional Honeycomb-Like Cu$_{65}$Co$_{10}$O$_{42}$ Nanoparticles on Nickel Foam as a High Efficient Oxygen Evolution Electrode for Anion Exchange Membrane Electrolyzer
Kyu Hwan Lee1,2, Myeong Je Jang1,2, Woo-Sung Choi1, Yoo Sei Park1, and Sung Mook Choi1; 1Korea Institute of Materials Science, Gyeong Nam, Korea (the Republic of); 2Advanced Materials Engineering, Korea University of Science and Technology (UST), Changwon, Korea (the Republic of).

Anion exchange membrane (AEM) electrolyzer is based on PEM electrolyzer combined with an anion exchange membrane (AEM) in the middle of cell. AEM electrolysis provides benefits of both PEM membrane (acidic) and traditional liquid alkaline (KOH) electrolysis with efficiency likely in between these two existing technologies. Although the most important benefit of AEM is possibility of adapting non-PGM catalysts, low activity of those catalysts remain still big challenges.

In this presentation, we prepared three-dimensional honeycomb-like Cu$_{65}$Co$_{10}$O$_{42}$ nanoparticles arrays supported by Ni foam via electrochemical co-deposition of Co and Cu hydroxides on Ni foam followed by thermal oxidation. The co-deposition with Cu changes the morphology of the Co hydroxide deposit to form honeycomb-like nanostructures, significantly decreasing the onset potential for oxygen evolution. The Cu$_{65}$Co$_{10}$O$_{42}$ anode displays an exceptionally low overpotential of 290 mV at a current density of 10 mA cm$^{-2}$ in 1 M KOH, and an anion exchange membrane water electrolysis cell employing the above anode achieves a current density of 100 mA cm$^{-2}$ at 1.68 V in 0.1 M KOH.
When in amorphous form (a-TMD), these materials have even higher activity, thanks to their disordered structure with a high density of under-coordinated sites. However, the structure-performance relationship is unknown and traditional synthesis methods do not grant precise control over the deposited morphology, usually resulting in unsatisfactory HER performances for self-supported a-TMD.

In this contribution, we explore a HER performance/structure correlation for self-supported amorphous TMD catalysts, focusing on amorphous Molybdenum Sulphide (a-MoS₂), Molybdenum Selenide (a-MoSe₂) and Tungsten Selenide (a-WSe₂). We couple the intrinsic high activity of amorphous materials with a precise control over the morphology of the synthesized catalysts, obtained by utilizing Pulsed Laser Deposition (PLD) as synthesis method. In this way it is possible to control down to the nanoscale the structure and the morphological features of the materials, obtaining structures that range from compact films to hierarchical nanostructured morphologies.

We firstly analyse the shared electrochemical activation process, occurring at the beginning of catalysis, where the pristine a-TMD are transformed into the actual HER catalysts. Pre/post characterization is employed to evaluate how the activation modifies the composition and the catalytic performance. We find that the effect of the activation process on the electrochemical performance is related to the different transition metal (i.e. Mo or W) in the a-TMD.

By tuning the morphology of the a-TMD, we maximize the Tafel slope value and the -10 mA cm⁻² overpotential ($\eta_{10}$). The optimized morphologies reach HER performances among the state-of-art for TMD materials, regardless of their support or crystalline structure. For a-MoS₂, a Tafel slope of 35 mV dec⁻¹ – close to the Pt benchmark of 30 mV dec⁻¹ – and a -10 mA cm⁻² overpotential ($\eta_{10}$) of 126 mV are obtained, while for a-WSe₂, a $\eta_{10}$ of 196 mV is registered.

In conclusion, by controlling during the synthesis process the a-TMD nanostructures’ morphology we show the correlation between structure and HER performance, that is reflected by the relation between morphological features and intrinsic HER catalytic parameters, such as charge transport efficiency and onset potential; moreover, we exploit this correlation on materials with intrinsic high activity, obtaining catalysts that with their performances provides a promising alternative to precious catalysts.

9:00 AM *ES06.06.04
Tracking and Identifying the Active Origin in Chalcogenide Catalysts for Electrochemical Hydrogen Evolution Jiangtian Li and Deryn Chu; U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Water electrolysis has been emerging as a strategic approach to produce hydrogen, especially with the clean and renewable energy sources like solar and wind. To this end, the design, development, and fabrication of facile, active, stable earth abundant electrocatalysts for highly efficient hydrogen evolution reaction are essential. In this presentation, we will show a bunch of electrochemical catalysts we recently developed for the hydrogen generation. We experimentally demonstrate the facet-dependent HER activity and the interfacial dipole enhanced HER activity in chalcogenide based catalysts. With the assistance of synchrotron radiation characterization techniques, we were able to track and identify the changes in the local atomic environments, and reveal and establish structure/function relationship in a catalyst. This could be coordinated with the HER performance and provide fundamental understanding on the reaction mechanism.

9:30 AM *ES06.06.05
An Efficient Acid-Stable N₂-Plasma Treated Hafnium Oxyhydroxide Electrocatalyst for Hydrogen Evolution and Oxidation Reactions Xiaofang Yang and Bruce E. Koel; Princeton University, Princeton, New Jersey, United States.

Lack of a highly active, stable, earth-abundant electrocatalyst for carrying out hydrogen evolution and oxidation reactions (HER and HOR) in strongly acidic conditions is a major technical challenge for developing economical polymer electrolyte membrane (PEM)-based electrolyzers and fuel cells. We have found that processing Hf oxide with an atmospheric N₂ plasma forms an acid-insoluble hafnium oxynitride material. We propose that under electrochemical environments this material is transformed into an active oxynitride hydrate that demonstrates unprecedented high catalytic activity and stability for both HER and HOR in strong acidic media for earth-abundant materials. The zero overpotential and high current densities demonstrate that this material is a promising alternative to Pt. This material demonstrates excellent HER and HOR activities in acids using non-platinum group metal (PGM) catalysts, opening new opportunities to develop technologically and economically viable regenerative fuel cell (URFC) systems and cost-effective PEM electrolyzers. Furthermore, these results have broad implications for using nitrogen incorporation (e.g. by N₂ plasma treatment) to activate other non-conductive compounds and films to form new active electrocatalysts.

10:00 AM BREAK

SESSION ES06.07: Nanoscale Characterizations
Session Chairs: Oliviero Andreussi and Wenchao Sheng
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 122 C

10:30 AM ES06.07.01
Nonprecious Electrocatalysts for Hydrogen Evolution via Water Electrolysis Shuo Chen; University of Houston, Houston, Texas, United States.

Water electrolysis produces hydrogen gas with high purity and no greenhouse gas emission. Large-scale applications of water electrolyzers require low cost, efficient, and stable electrocatalysts. In this presentation, I will introduce our recent efforts on nonprecious electrocatalysts for both cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER) of water electrolysis. Our best electrolyzer can reach current densities of 500 and 1000 mA cm⁻² at 1.586 and 1.657 V, respectively. To understand and better design the electrocatalysts, we employed density functional theory calculations to reveal active sites and their roles in water activation and hydrogen adsorption.

11:00 AM ES06.07.02
Atomic-Level Insights into Platinum Group Metal-Free Electrocatalysts Derived from Metal Organic Frameworks David Cullen 1, Karren More3, Gang Wu2, Deborah Myers1, K.C. Neyerlin4, Hoon T. Chung1 and Piotr Zelenay2; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2University at Buffalo, The State University of New York, Buffalo, New York, United States; 3Argonne National Laboratory, Lemont, Illinois, United States; 4National Renewable Energy Laboratory, Golden, Colorado, United States; 5Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The search for low-cost electrocatalysts to drive the oxygen reduction reaction (ORR) in polymer electrolyte membrane fuel cells has intensified with the recent deployment of commercial fuel cell electric vehicles. Platinum group metal-free (PGM-free) catalysts may offer a solution to using standard Pt-based catalysts if their activity and durability can be significantly improved. Breakthroughs in atomically-dispersed transition metal (Fe, Co, Mn) catalysts derived from metal organic frameworks (MOFs) have demonstrated improved performance and durability in fuel cell tests. It is expected that an increased understanding of the atomic-level structure–property relationships in PGM-free catalyst systems will enable further enhancement of these recent gains.

To this end, we have utilized in situ low-voltage, aberration-corrected scanning transmission electron microscopy (ac-STEM) coupled with quantitative analytical techniques such as electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) to study the structural evolution of MOF-derived catalysts at various stages of synthesis and fuel cell testing. The high spatial resolution (sub-Å) of ac-STEM allows for direction visualization of the catalytically active sites, which take the form of metal-nitrogen moieties within or at the edges of the meso-graphitic carbon support particles. We will present a quantitative analysis of the evolution in composition and support graphitization during high temperature pyrolysis (up to 1100°C) for catalysts containing Fe, Co, and Mn. The effects of metal loading and the negative impact of metal clustering on performance will be demonstrated. The critical role of support graphitization in the formation of the highly activity metal-nitrogen sites and electrode durability will also be explored. High-resolution microscopy results will be correlated with other advanced characterization methods, including synchrotron-based scattering techniques, and discussed within the context of fuel cell performance and durability to provide a more complete view of the materials-based mechanisms that control the electrochemical performance of
Titanium dioxide, or titania, is an important material being researched for energy and environmental applications, chiefly photocatalysis. Titania’s photocatalytic properties allow it to be used in water-splitting, detoxification, and photovoltaics. Titania exists in multiple polymorphic structures, of which the most common are rutile and anatase. We focused on anatase for the purposes of this research, due to its promising results for hydrolysis.

Anatase is a non-stoichiometric oxide (TiO$_2$) which enables it to perform redox reactions by absorbing and releasing oxygen into its environment. When this happens, oxygen vacancies form within the anatase lattice. In situ electron microscopy can provide a window into these structural changes taking place in anatase during photocatalysis. However, to correctly interpret vacancy induced structures and evolution from TEM imaging, it is necessary to compare the experimental images with simulated structural models.

Here we model the oxygen vacancy structures in anatase, using a combination of molecular dynamics and density functional theory. Using a forcefield designed for the simulation of titania-water interactions, different vacancy structures were relaxed and analyzed. To compare the theoretical models with experimental data, TEM image simulation was performed. We investigate a series of different vacancy configuration and generated TEM fingerprints for comparison with the experiment. This comparison yielded results which demonstrate a proof of concept for a technique suggesting that it should be possible to identify oxygen vacancy structures directly from the TEM image contrast.

The effect of surfaces on vacancy structure, and the interaction of water with the surface of anatase will also be examined. This research aims to satisfy an unfilled niche in our atomic-level understanding of oxides, by providing the methodology for analysis of vacancy formation from very subtle phenomena in TEM images.

References:

SESSION ES06.08: Computational Methods
Session Chairs: Ismaila Dabo and Jim Santivich
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 122 C

1:30 PM *ES06.08.01
Continuum Models to Handle Electrolyte Solutions Effects in First-Principles Simulations of Materials

Oliviero Andreussi; University of North Texas, Denton, Texas, United States.

Continuum models of solvation have played a crucial role in quantum chemistry simulations and are now starting to be popular for the computational characterization of solvated, possibly electrified, interfaces. Some recent advances in the field have opened the possibility of modeling heterogeneous catalysis and electrochemistry in a first-principles-based framework, where the multiscale nature of the developed approaches provides a significant reduction of the computational burden while retaining a good accuracy. Nonetheless, extending continuum approaches to condensed-matter simulations present some non-trivial issues, related to the complexity of the electrostatic problem in charged two-dimensional interfaces and to the open structure of many crystalline substrates. Here we will present some of our recently proposed approaches to overcome these limitations, in particular focusing on a hierarchy of approaches and algorithms to describe the electrochemical diffuse layer. Moreover, handling environment (solvent and electrolyte) effects through the continuum embedding allows us to exploit a more rigorous grand canonical approach to study the thermodynamic properties of electrochemical interfaces, thus overcoming some possible limitations of the computational-hydrogen electrode (CHE) technique. Applications to noble metal (electro-)catalysis and beyond will be presented.

2:00 PM *ES06.08.02
First-Principles Discovery and Understanding of Materials for Renewable Hydrogen Production

Brandon Wood1, Yuanyue Liu2, Tadashi Ogitsu2 and Tuan Anh Pham2; 1 Lawrence Livermore National Laboratory, Livermore, California, United States; 2 The University of Texas at Austin, Austin, Texas, United States.

Despite significant promise as a clean and sustainable energy carrier solution, today’s low-cost hydrogen is conventionally produced from fossil fuels. A far more attractive alternative involves the use of abundant renewable solar and wind energy, which provide avenues for producing hydrogen from water, either indirectly through electricity generation and electrolysis, or else directly through solar photochemical and photoelectrochemical processes. However, these new avenues introduce significant materials...
challenges, prompting the use of computational methods for aiding discovery, understanding, and optimization. To this end, I will review some of our recent simulation activities within the U.S. Department of Energy HydroGEN Advanced Water Splitting Materials Consortium, which aims to accelerate the development of materials for renewable hydrogen production from water. Focusing on the use of first-principles computational methods, I will provide examples of how atomic-level understanding of chemical bonding in 2D materials has been applied towards the discovery of new hydrogen evolution electrocatalysts. I will also show how simulations have been combined with in situ experiments to understand atomistic mechanisms of water splitting at photoelectrochemical interfaces, leading to novel approaches for improving device lifetime and performance. These successes demonstrate the power of computational methodologies for translating atomic-level understanding into practical solutions for renewable hydrogen production.

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

2:30 PM *ES06.08.03
First-Principles Studies of Activity and Selectivity in the Electrocatalysis of CO2 Reduction into Methanol  
Jianguo Yu, Yipeng Gao, Dong Ding, Hanping Ding, Lucun Wang and Wei Wu; Idaho National Laboratory, Idaho Falls, Idaho, United States.

Despite an extensive interest in developing advanced direct electrochemical reduction of CO$_2$ into value-added fuels and specialty chemicals using renewable energy as an input, its application is still constrained partly due to the fundamental challenges related to activity and selectivity towards the particular product of interest. Detailed first principles calculations are invaluable in complementing the experimental investigations to unravelling important aspects of the electrochemical reduction reaction mechanisms for various type of catalysts. Here, we present advances in the understanding of reactivity and selectivity in the electrocatalysis of converting CO$_2$ into methanol using density functional theory and thermodynamics. We will also discuss the role of protons and electrons transfer, and possible processes through different surface-bound reaction intermediates in order to steer catalyst selectivity among the vast number of possible carbon-based products.

2:45 PM *ES06.08.04
MXene Electrode Materials for Electrochemical Energy Storage—First-Principles and Grand Canonical Monte Carlo Simulations  
Yasauki Okada, 1 Nathaniel Keilbart, 2 James Goff, 2 Shin ‘ichi Higai, 1 Kosuke Shiratsuyu 1 and Ismaila Dabo 2; 1Murata Manufacturing Co., Ltd., Nagaokakyo-shi, Japan; 2Department of Materials Science and Engineering, Materials Research Institute, and Penn State Institutes of Energy and the Environment, The Pennsylvania State University, University Park, Pennsylvania, United States.

MXene compounds are drawing attention due to their advantageous characteristics, including the large surface area of their two-dimensional structure, which may enable high energy density for electrochemical storage. These compounds have the generic formula M$_{1-x}$Ti$_x$(X, T)$_y$, where M, X, T$_x$ represent the transition-metal cation, the carbon or nitrogen atom, and the surface termination of MXene layers, respectively. Since the discovery of MXene in the laboratories of Barsoum and Gogotsi, a number of studies have shown applications of their catalytic, electronic, mechanical, and optical properties [1,2]. In parallel, first-principles simulations have delivered quantitative information about their electrochemical response [3,4,5]; however, there is still debate over the charge-transfer mechanisms at the origins of electrochemical storage in MXene-based pseudocapacitors. In particular, it is still not fully understood how charge transfer is affected by transition-metal chemistry, stoichiometry, and surface termination. In the present study, we performed first-principles calculations on MXene compounds with 12 different transition metals (Sc–Cr, Y–Mo, La, and Hf–W), three different composition ratios (M$_x$X$_{1-x}$T$_y$, and M$_x$X$_{1-y}$T$_z$), and two different terminal groups (oxygen and fluorine). It was found that the electronic structures, formation energies and the amount of charge transferred from the cations to the MXene electrode is dependent on composition and that their charge is stored in the bond between the MXene and adsorbing cations. Importantly, the Bader atomic charge analysis revealed that the changes in valence number of the M-elements and X-elements are rather small, while the terminal groups play an important role in the pseudocapacitive charge storage of MXene compounds. Additionally, we carried out grand canonical simulations using a dataset of first-principles free energies, taking into account solvation effects using implicit solvent models based on the self-consistent continuum solvation (SCCS) formalism and including configurational entropy contributions via finite-temperature Monte Carlo sampling in an effort to clarify the charge storage mechanisms underlying the operation of the pseudocapacitive electrode [6]. We provide a detailed description of the sequence of desorption steps at the MXene surface as the applied voltage increases. Moreover, changes in the valence state and projected density of states were observed during the cation desorption reaction. These results provide design principles to improve the performance of MXene as an electrode material for electrochemical energy storage and to assess the electrochemical stability of MXene-based electrocatalyst under applied voltage and controlled pH.

(References)

3:00 PM BREAK

SESSION ES06.09: New Electrocatalytic Materials
Session Chairs: Ismaila Dabo and Jin Suntivich
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 122 C

3:30 PM *ES06.09.01
Metal Phosphide Catalysts for Low Temperature Fuel Cells and Beyond  
Scott Grever; Wake Forest University, Winston Salem, North Carolina, United States.

We have demonstrated the use of metal phosphide nanoparticulates (MPNs) as catalysts for key processes (oxygen reduction, formic acid oxidation, methanol oxidation) in low temperature fuel cells and in the related applications of CO$_2$ reduction and hydrogen peroxide production via oxygen reduction. At a basic level, we show that MPNs analogs of well-known metallic fuel cell catalysts such as Pd show significant improvements in stability and activity per mg of catalyst. Further, the P atoms can act to tune the metal atom charge density as demonstrated for AgP$_2$ catalyzed CO$_2$ reduction, where experiment and density functional theory both show a large decrease in overpotential for CO production compared to Ag, again with improved stability.

However, the strongest improvements are observed for systems in which the dilution of the metal atom on the surface completely alters the coordination of the adsorbed species. This is demonstrated in our recent work developing CoP$_2$, CoP$_3$, and CoP$_4$ as HER and ORR catalysts, where increased P content decreases the overpotential for HER to near the level of the Pt benchmark. DFT shows that sites with low absolute free energies of H adsorption are associated with single coordinating binding or highly strained bridge sites. Of interest is the extent to which MPNs can act as analogs to single atom catalysts, with initial results suggesting oxygen reduction by PnP$_2$ NPs generates hydrogen peroxide, similar to single atom Pt catalysts and unlike traditional Pt NPs.

4:00 PM *ES06.09.02
Synthesis and Electroanalytical Characterization of Binary and Ternary Sulfides for the Conversion of CO2 and CO to Methanol  
Jesus M. Velazquez, 1 Joseph Perryman, 2 Jessica Ortiz 1, Sarah Jones 2, Forrest Hyler 1, Joshua Jude 1, Aparva Melta 2, Ryan C. Davis 3, Anbarish Kulkarni 2 and Christopher Patridge 2; 1University of California, Davis, Davis, California, United States; 2Pomona College, Claremont, California, United States; 3SLAC National Accelerator Laboratory, Stanford, California, United States; 4D’Youville College, Buffalo, New York, United States.

Development of materials that can feasibly solve the growing dichotomy of simultaneously increasing energy demands and carbon emissions is an imperative that has become
uniquely important for current research efforts. An emerging avenue in this regard is the conversion of vastly abundant renewable energy sources that can be harnessed and directed towards synthesis of traditionally fossil fuel-based products from atmospheric feedstocks like CO₂. In order to translate such an energy conversion process into a viable technology, it is critical that design principles of selective electrocatalyst materials be elucidated in order to mitigate operating costs and improve overall process efficiency.

Results that will be presented herein, focuses on structure—function correlations across three versatile classes of transition metal chalcogenide materials, including metal dichalcogenides (MX₂; M = Mo, W; X = S, Se) Chevrel-phase sulfides (CPs) (MₓMoₓSₓ; M = transition or alkali metal; x = 0–4), and thiospinels (AB₂X₄; A = Cu, Mg; B = Ti, V, Cr; X = S, Se). These chalcogenides were found in our preliminary work to display exceptional promise as CO₂R catalysts. As such, the compositional, structural, and dimensional tunability of these classes of compounds will allow for development of structure—function correlations and design rules. Furthermore, we have identified CPs as selective towards the electrochemical reduction of CO₂ and CO to methanol (major liquid product) under an applied potential of -0.4 V vs RHE. Moreover, CPs such as Cu₂Mo₆S₈ exhibit an interesting electronic structure-function correlation founded on the basis of X-ray absorption spectroscopy. We correlate the selective electrochemical reduction of CO₂ and CO to methanol due to the potentially increased reactivity of the chalcogen species to the filling of 3p orbitals by metal promoters such as Cu, Ni, and Cr. It is suspected that CO₂ hydrogenation will be the rate-limiting step in the CO₂R to liquid fuels, hence being able to surmount the energy barrier associated with this step will rely strongly on the ability of the catalyst to facilitate hydrogenation. These reactive chalcogenides neighbor susceptible active sites (Mo) for CO binding, and so the overall reduction of CO₂ and CO to methanol through a CO hydrogenation mechanism is likely enhanced by the presence of an electron-donating species like a transition or alkali metal.

4:30 PM ES06.09.03

Electrochemical Conversion of CO₂ into C₂ Products at Anion Vacancy of Transition-Metal Dichalcogenides—A Computational Mechanism Study and Material Screening

Sungwoo Kang¹, Youngho Kang² and Seungwu Han³; ¹Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, Seoul, Korea (the Republic of); ²Materials Data Center, Korea Institute of Materials Science, Changwon-si, Korea (the Republic of).

The electrochemical carbon dioxide reduction (CO₂R) has been received large attention in converting CO₂ into valuable chemical species. For practical application of CO₂R, a catalyst with low overpotential and selectivity for the desired product is required. In general, C₁ species such as CO and HCOOH are mainly produced on the catalyst at the cathode. Production of multi-carbon (Cₙ) species such as ethanol and n-propanol can achieve higher economic value when produced with optimized current density, Faradaic efficiency (FE), and overpotential. Recently, Francis et al. demonstrated that MoS₂ converts CO₂ into 1-propanol as a major product for CO₂R at onset potential of ~0.5 V vs RHE.[1] It is also reported that the current density decreases when increasing the portion of edge sites, which implicates that the active site places on the basal plane rather than the edges. Despite the fact that MoS₂ produces 1-propanol, which is a highly valuable product, practical utilization of MoS₂ is limited because FE of CO₂R is only about 5% because of the poor selectivity compared to hydrogen evolution reaction (HER).

In this work, we first study the mechanism of CO₂R at sulfur vacancy (Vₖ) of MoS₂ by calculating free energies through the density functional theory calculations and computational hydrogen electrode model. We find several pathways leading to C₂ products such as HCOOH, HCHO, CH₃OH and CH₄. C₃ and C₄ pathways are discovered considering C-C coupling among C₁ intermediates. We want to note that HCHO is found to be a key intermediate for C₂ and C₃ pathways by coupling of sp² carbons. The computationally predicted reaction products and corresponding onset potentials are in good agreement with the experiment, which leads to the conclusion that Vₖ is the main active site of CO₂R on MoS₂. To discover a material producing C₂ products with better selectivity than MoS₂, computational screening of the catalytic performances of CO₂R is performed for anion vacancies of various transition-metal dichalcogenides (TMDs). As a result, TaS₂ and SnSe₂ are suggested as good candidates that can convert CO₂ into CO and HCHO, respectively, with much higher selectivity compared to MoS₂. Especially, we expect that production of HCHO at 5e-vacancy of SnSe₂ possibly leads to the production of C₃ products.


4:45 PM ES06.09.04

PBI-Type Polymers and Acidic Proton Conducting Ionic Liquids—Conductivity and Molecular Interactions

Jingjing Lin, Jürgen Griffin, Klaus Wippermann and Carsten Korte; Institut für Energie- und Klimaforschung (IEK-3), Forschungszentrum Jülich, Juelich, Germany.

The operation of polymer electrolyte fuel cells (PEFC) at elevated temperatures above 100°C would allow a much simpler system setup: i) no feed gas humidification, ii) a more efficient cooling system (easier water and heat management), iii) the possibility of recovering high-grade waste heat, and iv) a higher tolerance against feed gas impurities. Currently, (high temperature) HT-PEFC, based on phosphoric acid doped polybenzimidazole (PBI) membranes, cannot compete with the performance characteristics of NAFION-based low temperature-PEFCs. The presence of H₃PO₄ causes a slow cathodic oxygen reduction reaction kinetics (ORR). Thus, there is a necessity for new non-aqueous proton conducting electrolytes operational for the temperature range between 100–120°C.

Proton conducting ionic liquids (PILs) with acidic cations are promising candidates for the use as non-aqueous electrolytes at operation temperatures above 100 °C. In this contribution, an experimental study on the interaction of PBI based proton exchange membrane (PEM) with highly acidic betaine-type PILs is presented. 2-Sulfoethylmethylammonium triflate exhibits a ~3 times higher ORR current densities on Pt compared to H₃PO₄.[1] There is a (slow) uptake of the electrolyte by PBI due to a swelling process, up a weight increase of 135%. The doping process was monitored by Raman spectroscopy, proving the protonation of the imidazole groups in the polymer chains. The thermal stability is measured by TGA.

NMR analysis and inelastic neutron scattering has been applied to elucidate the proton dynamics and the molecular interactions between PIL, PIL, and residual water, which is present during fuel cell operation. The total conductivity in the neat PILs depends highly on the H₂O concentration. The high acidic PILs are able to protonate H₂O. The self-diffusion coefficients are measured by DOSY NMR, revealing that the proton diffusion is faster than the diffusion of the PIL cation. The above results indicate a cooperative mechanism involving fast proton exchange between PIL cations, H₂O and H₃O⁺.

Compared to the neat PIL, the proton conduction in the doped PBI membrane is restricted due to the constraining network of the polymer chains. To optimise the conductivity but also the uptake of the PIL into the polymer, the use of solution casting methods have been studied for these materials.


SYMPOSIUM ES07

New Carbon for Energy—Materials, Chemistry and Applications

April 23 - April 25, 2019

Symposium Organizers

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* Invited Paper
Sustainable Noble Metal-Free Electrocatalysts for Fuel Cells and Electrolyzers Sanjeev Mukerjee and Qingying Jin; Northeastern University, Boston, Massachusetts, United States.

Enabling concerted charge transfer at the inner Helmholtz plane of an electrochemical interface is a prelude to higher selectivity and activity for electrochemical processes hitherto not possible with conventional highly dispersed metal and metal alloy electrocatalysts. This presentation will focus on recent shifts away from conventional supported metal and metal oxide based catalysts to organo-metallic and composite metal oxides based structures, which promise orders of magnitude higher turnover frequency and selectivity. Taking oxygen reduction and hydrogen evolution reactions (ORR/H2R) as a theme, this presentation will provide a clear comparison of electrochemical response between supported metal catalysts (alloys and oxides), especially carbon supported noble metals in acidic pH and catalyst based on transition metal nitrogen coordinated systems and multi-phase composite oxides. Electrochemical data will be discussed in the context of spectroscopy, especially in situ synchrotron x-ray absorption spectroscopy (XAS). Here the conventional bulk averaged XANES and EXAFS spectroscopy will be further embellished by the unique use of the subtractive method referred to as ‘Δμ technique’. This specially designed subtractive technique using the near edge part of the spectra (x-ray absorption near edge spectra, XANES) has been previously validated and has unprecedented ability to elucidate nature of adsorbed species on transition metals. The unique element specificity and the in situ and operando capability of the XAS spectra in close conjunction with electrochemical data will be used to provide insight on steady-state electrocatalytic pathways as a function of various operating conditions and associated applications. Unique structural features of the active sites determined in situ using the extended part of the spectra (i.e., extended x-ray absorption spectra, EXAFS) will be invoked to explain activity difference based on pH and water activity.

Searching for the Active Site in Carbon-Based Noble Metal-Free Oxygen Reduction Electrocatalysts Piotr Zelenay1, Siddharth Komini Babu2, Hoon T. Chung1, Ulises Martinez1, Xi Yin1, Edward F. Holby2 and Geraldine M. Purdy1; 1Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2Sigma Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

The focus of this presentation will be on carbon-based noble metal-free or, as they are often called, platinum group metal-free (PGM-free), electrocatalysts for oxygen reduction reaction (ORR) as an alternative to the state-of-the-art low-PGM catalysts in the polymer electrolyte fuel cell (PEFC) cathode. In the past decade, PGM-free catalysts, especially those obtained by heat-treating precursors of transition metals, nitrogen and carbon, have gradually narrowed the performance gap to precious metal-based materials already used in fuel cell cars. We start by reviewing PGM-free catalyst development at Los Alamos National Laboratory (LANL), part of the DOE-EERE’s Electrocatalysis Consortium (ElectroCat), emphasizing approaches aimed at improving the ORR active-site density and electrode porosity via the use of pore-forming agents and sacrificial templates.

In the second part of this presentation, we will specifically concentrate on the sources of catalytic activity in Fe-based PGM-free catalysts and ORR active sites as a prerequisite for successful development of future noble metal-free catalysts. While of key importance to further progress in PGM-free electrocatalysis, the identification of the ORR active sites in the catalysts is highly challenging due to their embedded nature within the carbon phase and highly heterogeneous catalyst morphology resulting from the high-temperature synthesis process. They make identification and improvement of activity and durability of such sites difficult and often ambiguous. The results from both theoretical modeling and experiment will be presented. Of a number of both in situ and ex situ techniques used for gaining a better insight into the origins of ORR activity in PGM-free catalysts, we will concentrate on the microscopic and X-ray absorption spectroscopic methods, as well as on the implementation of molecular dioxygen analogues as probes for the ORR active sites on the catalyst surface, which makes otherwise bulk techniques surface-specific. This part of the presentation will include research performed in close collaboration with LANL’s ElectroCat partners.

Time permitted, we will report on the activity and durability of catalysts derived from transition metals other than Fe, specifically, Co, Mn and Ni, studied by using once again both modeling and experimental methods. Finally, we will present a few highlights from a continuing comparative study of the degradation of active sites in noble-metal-free catalysts during fuel cell testing.

Carbon-Based Materials for Electrochemical Transformation in Energy Conversion and Storage—Defects or Not? Yuyan Shao, Xiaohong Xie, Huilin Pan and Jun Liu; Pacific Northwest National Laboratory, Richland, Washington, United States.

In this talk, we will present our recent research on carbon-based electrode materials for oxygen electrocatalysis (related to fuel cells) and sulfur transformation (related to metal-S batteries). We investigate elemental doping (including metals, N, O, ... ) on carbon properties. Broadly speaking, all dopings produce structural or chemical defects in carbon. However, from practical application point of view, not all defects benefit electrochemical transformation reactions. Our research reveals that, while defects (with right composition and configuration) in general are positively related to oxygen electrocatalysis, defects (or functional groups) seem to be unfavorable for sulfur transformation in a battery under conditions relevant to real applications. We will discuss our understanding on defects vs. electrochemical transformation.


3. Wang, Xiaofei; Cullen, David; Pan, Yung-Tin; Hwang, Sooyeon; Wang, Maoyu; Feng, Zhenxing; Wang, Jingyun; Engelhard, Mark; Zhang, Hanguang; Yanghua He; Shao, Yuyuan; Su, Dong; More, Karen; Spendelow, Jacob; Wu, G. Nitrogen Coordinated Single Cobalt Atom Catalysts for Oxygen Reduction in Proton Exchange Membrane Fuel Cells, Advanced Materials, 30, 1707658, 2018.


2:00 PM *ES07.02.02 High-Throughput Synthesis and Characterization of PGM-Free Oxygen Reduction Electro catalysts for Polymer Electrolyte Fuel Cells Deborah Myers, Magali Ferrandon, Jaehyung Park, Nancy Kariuki, A. Jeremy Kropf and Evan Wegener; Argonne National Laboratory, Lemont, Illinois, United States.

Incredible progress has been made over the past decade in increasing both the oxygen reduction reaction (ORR) activity and durability of platinum group metal-free (PGM-free) polymer electrolyte fuel cell (PEFC) cathode catalysts. For example, electrocatalytic activities approaching those of platinum have been obtained with heated-treated iron-doped zelite imidazolate frameworks (ZIFs). With further improvements in these materials and electrodes based on these materials, especially in hydrogen-air performance and long-term performance durability, these materials will become viable for numerous applications, including automotive propulsion power. For the pyrolyzed iron-carbon-nitrogen class of PGM-free materials, it has been determined that variables such as the metal, polymer, and carbon content, as well as the temperature and atmosphere in which the composites are pyrolyzed are important in determining the activity and activity stability of the resulting catalysts. Changing these variables and testing their effect on the resulting catalyst properties is a very time-consuming process and only a limited portion of the composite composition and temperature space have been explored for this broad class of materials. This presentation will describe the development and application of high-throughput methodology to explore the effects of these parameters on the activity and fuel cell performance of iron- zelite imidazolate framework-derived ORR electro catalysts with a variety of transition metal dopants. A multi-channel flow double electrode (m-CFDE) cell was designed and constructed for the simultaneous screening the ORR activity of multiple materials using an aqueous hydrodynamic technique. The high-throughput structural characterization of the materials using techniques such as X-ray diffraction and X-ray absorption spectroscopy and correlation of the phase and atomic structure with ORR activity will be described as will the high-throughput testing and optimization of the electrode composition using a 25-electrode array fuel cell. In addition, the use of in situ multiple X-ray absorption spectroscopy to determine the atomic structure of the materials during pyrolysis of the precursors will be presented.

2:30 PM ES07.02.03 Conversion of Solar Power to Chemical Energy Based on Carbon Nanoparticle Modified Solar-Thermoelectric Generator and Electrochemical Water Splitting System Xiaofei Zhang1, 2, Zhijian Sun1 and Hong Liu1; Shandong University, Jinan, China; 1Georgia Institute of Technology, Atlanta, Georgia, United States.

Nanogenerator has caused extensive attraction to convert/collect dispersive energy as electric energy. Solar thermoelectric generator (STEG), based on Seebeck effect of semiconductors, is one of the most promising approaches for solar energy conversion because of its simple structure, high stability and long lifetime. The light absorbers are of paramount importance for high-efficient STEG. In this work, high performance carbon nanoparticles for light harvesting have been synthesized via a facile and efficient method. By the in-situ coating of the nanoparticles on a commercial thermoelectric generator, a high-efficient STEG was constructed. The performance of the designed STEG device can be further improved with the integration of heat preservation and heat sink components. There is 34 times higher efficiency than that of the bare commercial thermoelectric generator, which enables an electrochemical process to generate hydrogen gas by water splitting. Be a kind of nanogenerator, this designed STEG devices provide a cheap and facile strategy for the portable power supply.

2:45 PM ES07.02.04 Self-Assembly of Large-Area 2D Polycrystalline Transition Metal Carbides for Hydrogen Electrocatalysis Xingming Zhang1, Wenshu Chen2, Jiayuan Gu2, J. Nathan Holman3 and Liwei Lin4; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Shanghai Jiao Tong University, Shanghai, China; 3Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4University of California, Berkeley, Berkeley, California, United States.

Low-dimensional (0/1/2 dimension) transition metal carbides (TMCs) possess intriguing electrical, mechanical, and electrochemical properties, and they serve as convenient supports for transition metal catalysts. Large-area single-crystalline 2D TMC sheets are generally prepared by exfoliating MXene sheets from MAX phases. Here, a versatile bottom-up method is reported for preparing ultrathin single-crystal TMC sheets (=10 nm in thickness and >100 μm in lateral size) with metal nanoparticle decoration. A gelatin hydrogel is used as the scaffold to coordinate metal ions (Mo4+, W6+, Co2+), resulting in ultrathin-film morphologies of diverse TMC sheets. Carbonization of the scaffold at 600 °C presents a facile route to the corresponding MoC2, WC and CoC2, and to metal-rich hybrids (Mo4- xW6x and Mo4C–Co). Among these materials, the Mo4C–Co hybrid provides excellent hydrogen evolution reaction (HER) efficiency (Tafel slope of 39 mV dec-1 and 48 mV dec-1 in 1 M H2SO4 and 0.5 M H2SO4). Such performance makes Mo4C–Co a viable noble-metal-free catalyst for the HER, and it is competitive with the standard platinum on carbon support. This template-assisted, self-assembling, scalable, and low-cost manufacturing process produces a new tactic to construct low-dimensional TMCs with applications in various clean energy-related fields.

3:00 PM BREAK

3:30 PM *ES07.02.05 Pyrolyzed Metal-Nitrogen-Carbon Catalysts for Oxygen Reduction in Polymer-Electrolyte Fuel Cells Frederic Jaouen; UMR 5253, CNRS, Montpellier, France.

The oxygen electro-reduction reaction (ORR) is the cathode reaction in fuel cells, an electrochemical energy conversion device envisioned to replace combustion engines for transportation, and with stationary applications as well. While novel platinum nanostructures have allowed decreasing the amount of precious metal required to catalyze the ORR in proton-exchange membrane fuel cells, strong advances in the class of Earth-abundant metal-nitrogen-carbon (Me-N-C) catalysts has attracted a lot of attention. Synthesized above 700 °C, recent Me-N-C catalysts are the object of intense research regarding the nature/structure of their active site, ORR mechanism and stability in a variety of conditions. The electrolyte pH, electrochemical potential cycling, temperature, and presence of peroxide are recognized key factors that can influence the stability. This presentation will focus on novel understanding acquired on a recent set of Fe-N-C and Co-N-C catalysts comprising, in parallel with atomically-dispersed metal cations covalently attached to the N-doped carbon matrix, a controlled amount of metal-based crystalline structures, down to their complete absence. The synthesis of model Me-N-C catalysts and the coupling of electrochemical studies with spectroscopic techniques revealed important aspects of Me-N-C catalysts regarding the origin of their ORR activity and, perhaps even more importantly, on the fate of the metal-based active sites when subjected to a broad variety of stressing conditions. It will be shown how structure-stability relationship could be established in some cases, but also how unmodified metal coordination is a necessary but non-sufficient criterion for catalyst durability. Due to the intimate integration of the metal in the nitrogen-doped carbon matrix, changes in the physico-chemical properties of the carbon surface will be shown to impact the catalytic properties (activity and selectivity) of the metal-based sites. This will highlight the importance of the properties of the hosting carbon material on metal-based sites, in strong relation with the symposium topic.

4:00 PM *ES07.02.06 Graphite Electrodes for Potassium-Ion Batteries Shinichiro Komaba1, 2, Kei Kubota1, 2 and Hiroo Onuma1; 1Tokyo University of Science, Tokyo, Japan; 2ESICB, Kyoto University, Kyoto, Japan.

We have been studying electrode and electrolyte materials and their interface designs for Li-ion, Na-ion, and K-ion batteries [1]. Yearly paper numbers of Na and K batteries have increased drastically in recent years. Indeed, research and development of high-performance positive/negative electrode materials for Na- and K-ion are conducted actively over the world. Because of larger ionic size of potassium than lithium, much wider variety and unique feature of materials chemistry attract researchers' interests as post Li-ion battery. New carbons are of great importance for higher energy Na-ion and K-ion batteries. In this talk, we will present our recent studies on phase transition and electrochemical properties
of graphite electrode for K-ion batteries compared to some carbons for Li-ion and Na-ion batteries. [1] K. Kubota, S. Komaba et al., “Towards K-ion and Na-ion batteries as “beyond Li-ion,” Chem. Rec., 18, 459 – 479 (2018).

4:30 PM ES07.02.07
Impact of Surface Modification of Carbon Felt-Supported Pd Nanoparticles on Electrochemical Hydrogenation of Oxygenates
Abhi Karkamkar; Pacific Northwest National Laboratory, Richland, Washington, United States.

Electrochemical reduction of biomass-derived feedstocks is a critical need to improve conversion efficiencies without the need for generating molecular hydrogen. During an electrochemical hydrogenation (ECH) process, it is formed on the surface of the catalyst via reduction of protons supplied by the electrolyte, hydrogenating organic substrates. The feedstock derived from biomass is uniquely complex in composition and functionality. Solvents such as water and other organic solvents add an unprecedented level of complexity to the catalyst design and synthesis. Majority of the electrocatalytic reduction studies are mostly carried on simple but versatile electrocatalyst (Pt/K or Pt/C) that have shown superior activity in PEM fuel cells. There is a critical need to understand the impact of electrocatalyst structure and composition on enhancing conversion of biogenic substrates to fuels or intermediates. Here we present our recent progress in modification of carbon felt based electrocatalysts. We have developed synthetic protocols and methods to modify these carbon felt based materials by incorporating heteroatoms such N or O containing polymeric materials. We further engineer the nanostructure by utilizing inorganic structure modifiers to enhance surface area and porosity. We have demonstrated the ability to change the surface area from 2 m²/g to 110 m²/g. The effect of these modifications on incorporation of metal nanoparticles will also be presented with XPS techniques. The impact of these structural and chemical modification of the carbon felt based catalysts on electrocatalytic reduction of carboxyl compounds will be discussed.

4:45 PM ES07.02.08
Jacob D. Beley1, Deepan Kishore Kunjilar2, Bo-Rei Pas1, Hung-Kuei Chang3 and Nai-Chang Yeh1, 3Department of Chemistry, California Institute of Technology, Pasadena, California, United States; 1Institute of Materials Science and Engineering, National Central University, Taoyuan, Taiwan; 2Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 3Department of Physics, California Institute of Technology, Pasadena, California, United States; 4Kavli Nanoscience Institute, California Institute of Technology, Pasadena, California, United States; 5Department of Electrical Engineering, California Institute of Technology, Pasadena, California, United States.

Despite the advantageous properties, graphene has found limited use in practical applications due to the difficulty of producing appropriate graphene materials in high yield. In particular, a scalable synthesis of graphene materials would benefit electrochemical energy storage applications, i.e., batteries and supercapacitors, by virtue of graphene’s high electron mobility, allowing fast charging and discharging, and graphene’s high surface area, providing a high density of electrochemical active sites for better storage capacities. To overcome this barrier, we have developed a scalable synthesis of high quality vertical graphene nanostripes (GNSPs) via plasma enhanced chemical vapor deposition (PECVD). GNSPs are a class of vertical graphene nanostructures (VGNSs), wherein multilayer graphene sheets grow vertically with respect to the growth substrate. This vertical growth allows the graphene materials to be synthesized in high density affording the possibility of scalability, as compared to horizontal sheet graphene. However, typical VGN syntheses require several hours and temperatures in excess of 700 K. In contrast, our GNSPs synthesis is fast and room temperature. In addition, typical VGN syntheses produce short graphene sheets, whereas our GNSPs synthesis produces long aspect ratio graphene materials with dimensions such as 500 nm x 70 μm; long aspect ratios are particularly desired for electrochemical energy storage due to the superior electrochemical activity of graphene edges and the percolation effect of the high aspect ratio graphene that affords greater charge transport. To achieve fast and high quality growth of GNSPs we place a copper foil in a microwave-induced hydrogen/methane plasma under medium vacuum with trace contents of substituted benzene precursors (e.g., 1,2-dichlorobenzene, tolue, etc). The substituted benzene precursor both acts as a seed that initiates growth of the sp²-hybridized graphene lattice and further propagates growth of the vertical graphene materials. In addition, methane radicals and hydrogen radicals act to enhance growth and etch/remove defects, respectively, resulting in high quality graphene materials. Various characterizations have validated the high quality of our GNSPs. The Raman spectrum contains narrow peak widths and peak height ratios that suggest high quality graphene. X-ray photoelectron spectroscopy demonstrates a chemically pure material, ultraviolet photoelectron spectroscopy reveals a work function similar to pristine graphene, and four-point probe measures reveal high electron mobility. Furthermore, the defect content, dimensions and surface area of GNSPs can be tuned by adjusting the PECVD parameters such as the microwave power, flow rate, pressure, and gas composition. Practical application of graphene, particularly in the field of energy storage, may be achievable by this scalable growth of high quality GNSPs.

SESSION ES07.03: Poster Session I: Carbon-Based Materials in Energy Applications
Tuesday Afternoon, April 23, 2019
PCC North, 300 Level, Exhibit Hall C-E

ES07.03.02
Copper-Promoted Nitrogen-Doped Carbon Derived from Zeolitic Imidazole Frameworks for Oxygen Reduction Reaction
Yunchao Xie1, Chi Zhang1, Xiaoming He1, Jheng-Wun Su1, Thomas Parker1, Tommi White1, Mark Gries1 and Jian Lin1; University of Missouri-Columbia, Columbia, Missouri, United States; “Weapons and Materials Research Laboratory, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

Rational design of oxygen reduction reaction (ORR) electrocatalysts based on earth-abundant elements is critical important towards sustainable energy applications. Among various reported ORR electrocatalysts, transition metal-nitrogen doped carbon (TM-N/C) materials such as Fe-N/C and Co-N/C exhibit excellent catalytic activity. Nevertheless, comprehensive understanding of these TM-N/C electrocatalytic systems is still lacking, which demands extension of investigation to other TM-N/C systems (Cu, and Mn, etc). Herein, we developed a Cu promoted nitrogen-doped carbon (Cu-N/C) via high temperature pyrolysis of Cu-adsorbed zeolite imidazole frameworks (Cu@ZIF-8). The Cu-N/C electrocatalyst exhibited satisfactory ORR activity with half-wave potential of 0.813 V in 0.1 M KOH electrolyte. Moreover, it also showed excellent methanol tolerance and long-term stability. The enhanced ORR electrocatalytic performance is attributed to the strong synergistic effect between Cu(II)-N ligands and Cu catalysts, sufficient active sites, and fast mass transfer.

ES07.03.03
Rapid Synthesis of Zeolitic Imidazolate Frameworks in Laser Induced Graphene Microreactors
Yunchao Xie, Chi Zhang, Jheng-Wun Su, Heng Deng, Cheng Zhang and Jian Lin; University of Missouri-Columbia, Columbia, Missouri, United States.

To date, various approaches to synthesize zeolitic imidazolate frameworks (ZIFs) have been developed, such as solvothermal, sonochemical, microfluidic, and mechanochemistry reactions. However, most of them are time-consuming and involve complex processing steps, thus they cannot rapidly screen potential candidates to obtain ZIFs on demand. Such a challenge calls for efficient synthetic approaches. Herein, we overcome this challenge by employing two nonconventional heating strategies, i.e., microwave- and Joule-heating, which are induced by laser-induced graphene (LIG) microreactors, for rapidly synthesizing ZIFs. In the first reaction, the LIG acts as a susceptor that absorbs electromagnetic energy, which is converted to heat. In the later one, LIG acts an electrical conductor that converts electrical energy to heat. Both two can rapidly heat up the reactor, accelerating the crystal growth for synthesizing ZIFs with well controlled morphology and crystallinity. To demonstrate a conceptual application, a ZIF-67/LIG composite was converted to a CoCoN/C/LIG by a CO₂ laser induction process. It shows great oxygen reduction reaction (ORR) performance with a half-wave potential (E₁/₂) of 0.798 V, and superior methanol tolerance and long-term stability. These rapid and facile synthesis methodologies will enable to quickly optimize reaction conditions and fast screen compound libraries for searching new materials, paving a way to high-throughput and autonomous nanomanufacturing.

ES07.03.04
Nitrogen Doped Coal—A High Efficient Electrocatalyst for Oxygen Reduction Reaction
Chi Zhang and Jian Lin; University of Missouri Columbia, Columbia, Missouri.
United States.

It is of a great challenge to develop high efficient nonprecious electrocatalysts to replace Pt-based catalysts for oxygen reduction reaction (ORR). This study introduces a cost-effective and environmentally friendly ORR electrocatalyst based on nitrogen doped coal (NOC) via a pre-oxidation of raw coal followed by a urea assisted annealing process. The obtained materials show great electrocatalytic activity with the onset potential, half-wave potential, and diffusion-limited current density comparable to those of a commercial Pt/C catalyst. In addition, it follows a four-electron pathway and has relatively low peroxide yield. Finally, it exhibits a good stability and strong tolerance to methanol poisoning. A systematic characterizations illustrate that these great performance could arise from high graphitic N and pyridinic N contents, existence of trace metal elements, and porous structures in the synthesized NOC. The demonstrated high performance makes NOC a promising catalyst for applications in metal air batteries and alkaline fuel cells.

**ES07.03.06**

**Texture Controllable Hierarchical Porous Carbon as Flexible Electrode for High Rate Performance Supercapacitor**

Jiang Hedong and Chunyang Jia; University of Electronic Science and Technology of China, Chengdu, China.

Hierarchical porous carbon (HPC) as flexible electrode attracts enormous attention due to its favorable properties, which is advantageous for the improvement of supercapacitors capacitance and rate capability. In this research, texture controllable HPC flexible electrode with high capacitive performance is successfully prepared by polymerization induced phase separation method. Solvents with various viscosities and hydroiodic acid with various amounts are used to regulate the texture. Scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), nitrogen adsorption and desorption isotherms, density functional theory (DFT) method are used to characterize or modelling the morphology, micro-pore, specific surface area and pore size distribution, respectively. The desired hierarchical porous structure endows the carbon material with a high specific surface area and ideal transportation paths. The optimized HPC flexible electrode reaches a high specific capacitance of 142.9 F g\(^{-1}\) at 1 A g\(^{-1}\) in a two-electrode configuration in 6 M KOH, which is 79.1\% of the capacitance measured at 0.2 A g\(^{-1}\). Furthermore, energy density of the supercapacitor device ranges from 6.27 Wh kg\(^{-1}\) to 4.23 Wh kg\(^{-1}\) with the power density ranges from 100 W kg\(^{-1}\) to 46195 W kg\(^{-1}\).

**ES07.03.07**

**Soft-Templated Tellurium-Doped Mesoporous Carbons as a Pt-Free Electrocatalyst for High-Performance Dye-Sensitized Solar Cells**

Chang Ki Kim and Hwan Kyu Kim; Korea University, Sejong City, Korea (the Republic of).

In recent years, research into sustainable and renewable energy resources has attracted much attention due to the increase in concerns about the energy crisis, decreasing availability of fossil fuels and environmental issues. From these points of view, photovoltaic technologies are a highly desirable solution because clean solar energy is supplied indefinitely by the sun. Among various photovoltaic devices, dye-sensitized solar cells (DSSCs) are some of the most promising energy conversion devices because of their low fabrication cost, environmentally friendly nature and high conversion efficiency. Generally, DSSCs consist of four important components: an n-type semiconductor photoanode, a sensitizer (dye), an electrolyte with an iodine or cobalt redox couple, and a counter electrode (CE). For the high performance of a DSSC device, optimization of all components is necessary. In particular, the CE is a very important component in the DSSC device, as it behaves as a catalyst for regeneration of oxidized electrolyte, as well as an electron collector from the external circuit. The use of rare metals such as Pt counter electrodes (CEs) is one major drawback of DSSC devices for broad real-life applications. In this regard, alternative materials to Pt CEs have been long sought for DSSC employing both cobalt and iodine redox couples. Therefore, in this study, soft-templated tellurium-doped graphene films were prepared by the simple pyrolysis of PAN-ht-PBA block copolymer in the presence of a tellurium precursor for replacing the Pt CE. To confirm the chemical composition and porosity, the as-prepared Te-SMC materials were evaluated by elemental analysis (XPS, EDS), and nitrogen sorption isotherm measurements. As-prepared Te-SMC materials contained mainly mesopores and retained three-dimensionally hierarchical graphite-like structure with many defect sites. They displayed doping levels with nitrogen of 9.15 atom % and tellurium of 0.15 atom % and had specific surface area of 540 m\(^2\) g\(^{-1}\). Therefore, these characteristics enabled the development of a high-performance CE in DSSCs with cobalt and iodine redox couples. As a result of its catalytic performance, Te-SMC exhibited outstanding electrocatalytic activity as well as a much better electrochemical stability than the Pt CE for both redox couples even after 1000 potential cycles. The results show that a maximum conversion efficiency of 11.6\% and 9.67 \% could be achieved under one sun illumination (AM 1.5 G) for SGT-021(Co(bpy))\(^{2+/-}\) and N719(I \(^{-}\)-based devices with Te-SMC CEs, respectively and these values are superior to the corresponding device with Pt-CEs.

**ES07.03.08**

**Multifunctional Metal Incorporated Graphene Aerogels for Energy Management Applications**

Sahibah Peranaathan,1 Krishna Murulidharan1,² Srinivasa Raghavan1,³ Douglas A. Loy4, and B.G. Potter1,5; 1Department of Material Sciences and Engineering, University of Arizona, Tucson, Arizona, United States; 2Department of Planetary Sciences, University of Arizona, Tucson, Arizona, United States; 3Department of Chemical and Environmental Engineering, University of Arizona, Tucson, Arizona, United States; 4Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona, United States; 5Department of Optical Sciences, University of Arizona, Tucson, Arizona, United States.

Lightweight carbon based aerogels are widely recognized as promising platforms for electronic, biomedical, energy storage and sensor applications. In this context, the ability to fabricate multifunctional graphene based aerogels with tunable properties is demonstrated in this work. In particular, using a unique coagulation technique, ultra-lightweight, chemically modified, mechanically robust, and electrically conductive reduced graphene oxide (rGO) aerogels were fabricated. The salient aspects of the fabrication process are (i) the incorporation of crosslinking metal cations, and (ii) self-assembly of rGO platelets in solution, giving rise to porous, mechanically robust 3D structures. Further, the controllable incorporation of metal ions within the rGO matrix provides distinct routes towards tuning the ensuing electrical, electrochemical, thermal, and mechanical properties. To illustrate the versatility of the fabricated aerogels, their applications as binder-free supercapacitor electrodes, thermal interface materials with exceptional thermal transport properties, and high electrical conductivity coatings will be discussed.

**SESSION ES07.04: Syntheses and Characterization of New Carbon-Based Materials**

**8:15 AM ES07.04.01**

**Iodine-Doped Graphene Films for High-Performance Electrochemical Capacitive Energy Storage**

Zhu Yucan and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

Recently, the fabrication of high-performance graphene films as electrode materials has become a research tendency for flexible energy-storage devices. Here, we successfully prepared iodine-doped reduced graphene oxide (r-GO) films with excellent capacitive performance by a simple and versatile technique of iodine steam doping. The iodine as an effective n-type dopant can enhance the electrical conductivity of graphene films by charge transfer process, further improving capacitive performance of the devices. The electrochemical properties of as-prepared r-GO films with different mass loadings were systematically and comprehensively studied. With the change of mass loading (1.5–6.7 mg cm\(^{-2}\)), the gravimetric specific capacitance of r-GO films remained almost variable at the studied range of current density, and finally can reach ~150 F g\(^{-1}\) at 0.2 A g\(^{-1}\) with 6 M KOH electrolyte, exhibiting the high utilization of electrode materials. With the increasing mass loading, supercapacitors based on the r-GO films show almost linear growth of areal specific capacitance at any current densities from 1 to 30 mA cm\(^{-2}\) (eventually reach ~524 mF cm\(^{-2}\) at 1 mA cm\(^{-2}\)) and nearly no decline of the rate performance. Additionally, we fabricated flexible all-solid-state supercapacitors, which also display excellent areal specific capacitance (~450 mF cm\(^{-2}\)), great cycling stability and favorable electrochemical stability. These results indicate that the fabricated r-GO films have a great advantage as electrode materials for flexible energy-storage devices.

**8:30 AM ES07.04.02**

**Single Walled B@I\(_3\) and Gd@I\(_3\) Nanotubes Encapsulated within CNT**

Leonard D. Francis; Department of Advanced Electron Microscopy, Imaging and Spectroscopy,
The hollow interior of CNTs provides a unique environment for the fabrication of novel morphologies by stabilizing novel phases within its cavity (1). Inorganic nanotubes are morphological counterparts of carbon nanotubes. The synthesis and structural elucidation of single walled nanotubes of inorganic compounds is still a challenge (2). In this work, we employ AC electron microscopy imaging and spectroscopy to study a novel morphology of BiI$_2$ and GdI$_2$ - SWNTs encapsulated within CNTs. Thus the single walled nanotubes of BiI$_2$ and GdI$_2$ phases in this study, are obtained by employing CNT as a nanotemplate. This method involves the capillary filling of BiI$_2$/GdI$_2$ within CNT, by annealing the BiI$_2$/GdI$_2$-CNT mixture above the melting point of BiI$_2$ (GdI$_2$). Aberration corrected electron microscopy and spectroscopy in combination with image simulations are employed to reveal the morphology, structure and composition of these nanotubes. A critical host internal diameter was estimated, for the formation of such single walled nanotubes, based on the electron microscopy images. First-principles density functional theoretical calculations were carried out to determine the stability and electronic properties of these BiI$_2$/GdI$_2$ nanotubes. The ultrahigh one dimensional morphology of BiI$_2$/ GdI$_2$ presented here could lead to novel physical properties and applications (3-5).

References

8:45 AM ES07.04.03 Functional Nanoporous Graphene@Metal-Organic Frameworks—Design, Synthesis, Properties and Applications Jayaramlu Kollebovina$^{1,2}$, Stepan Kmert$^1$, Roland Fischer$^2$ and Radek Zboril$^1$; $^1$Regional Centre of Advanced Technologies and Materials, Olomouc, Czechia; $^2$Inorganic and Metal-Organic Chemistry, Technical University of Munich, Munich, Germany.

Among the porous materials, the hybrid porous materials metal-organic frameworks (MOF’s) have attracted attention, due to their potential applications in various fields owing to their inherent qualities like high surface area, large pore volume, active metal sites with ordered and tunable pores. But MOFs have important challenges for practical or industrial applications like moisture stability, conductivity and micro pores. However, non-porous graphene sheets are becoming an inexpensive material, have been proven an outstanding matrix to support various materials, leading to advanced materials for electro catalysis and other energy-related application. Further, hybrids of MOF and Functional Graphene materials or GOMFs have collaborative properties like conductivity, large internal surface area with hierarchical pores and significant stabilities, which can exploit for the various energy and environmental applications. Herein, we would like to discuss, our recent research interest focused on the synthesis of various novel hybrid Graphene-MOF porous materials by different approaches. The structure and coordination environment thoroughly characterized by various microscopy and spectroscopy measurements. Depends on functional properties of these G/MOFs exploited for environmental oil spills separation from water, hydrocarbon separation and photo/electrochemical water splitting applications.$^{1-5}$


9:00 AM ES07.04.04 Self-Assembly Synthesis of Carbon Electrode Architectures for Energy-Related Applications Sheng Dai$^1$; $^2$Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^3$Department of Chemistry, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Enhancement in electrochemical energy storage resides in tailored nanotextures resulting from making electrode materials hierarchically nanoporous. The complex interplay of solvent and solute structure and dynamics at the charged interface, the transport of electrolyte ions into and out of the pores, the solvation/desolvation processes occurring in pores approaching bare-ion dimensions, and formation of interfaces via chemical reactions are all important parameters. Herein, several self-assembly synthesis methods for carbon composites as electrode materials for energy storage will be discussed. The objective of this talk is to demonstrate that mesoporous carbons derived from soft-template synthesis not only entail a high storage capacity but also, most importantly, can be made through self-assembly synthesis to have a significantly enhanced electronic conductivity and storage capacity. This enhanced electronic conductivity in 3D architectures is the key to providing high rate capability for the corresponding energy storage systems.

9:30 AM ES07.04.05 Science of Nitrogen and Boron Doped Electrically Conductive Ultrananocrystalline Diamond Thin Films and Applications to Energy Generation/Storage Devices Pablo Tirado$^1$, Jesus Alcántara$^2$, Elida I. de Obaldia$^3$, Rafael Garcia$^4$ and Orlando Aucillo$^5$; $^1$MSE, The University of Texas at Dallas, Dallas, Texas, United States; $^2$Facultad de Ciencias y Tecnologia, Universidad Tecnologica de Panama, Panama, Panama; $^3$Departamento de Investigacion en Fisica, Universidad de Sonora, Hermosillo, Mexico.

Ultrananocrystalline Diamond (UNCD) films are being investigated due to their unique combination of properties such as high wear resistance, highest hardness relative to any other film, lowest friction coefficient compared with metal and ceramic coatings, corrosion resistance, negative electron affinity, low work function, and high electrical conductivity for Boron (B) doped and nitrogen-grain boundaries incorporated UNCD films. The combination of these properties make doped UNCD films suitable for many applications like Li-ion batteries electrodes, corrosion resistant coatings for metal electrodes for electrolysis-based water purification, thermionic and field emission devices, and future high power electronic devices. B-UNC films are currently marketed by Advanced Diamond Technologies, but the drawback is that B doping is produced during film growth by hot filament chemical vapor deposition (HFCVD) involving B contamination of the chamber where the film is grown, which can be used only for growing B-doped UNCD or other diamond films. This presentation will describe the results from research and development of a novel process for B doping large area UNCD films by thermal diffusion after growth, thus eliminating the problem of B contamination of the diamond film growth chamber. The research focused on understanding the chemical, structural and electrical properties of the UNCD films before and after doping with B by thermal diffusion. The UNCD films were grown by Microwave Plasma Chemical Vapor Deposition (MPCVD) and HFCVD techniques on Si(100) Si substrate. Subsequently, 200-nm thick Spin on Dopant (SOD) coating containing B atoms was grown on the UNCD films. followed by annealing in an atmospheric oven to evaporate any excess solvent from the SOD film. Successive chamber evacuations and purges flowing N$_2$ were performed to minimize O$_2$ content in order to avoid the C-based UNCD film being etched by oxygen at the high temperatures needed for Boron diffusion. UNCD films were ultra-sonically cleaned with solvents to remove remaining SOD coating. -doped and as deposited UNCD films were characterized by Raman, XRD, SIMS, UPS, XPS and Hall effect measurements. Raman and XRD analysis confirm that there was no induced graphitization or damage in the UNCD films during the B diffusion process, while SIMS, UPS, XPS and Hall effect analysis confirmed B doping and correlation with changes in electrical properties. The B-doped UNCD films exhibit 10$^4$ Ohm.cm resistivity. We also explored the synthesis of UNCD films with nitrogen (N) atoms incorporation into grain boundaries, during HFCVD growth with Ar/CH$_4$/N$_2$/H$_2$ gas mixture flow, and observed that N-UNC films also exhibit 10$^4$ Ohm.cm resistivity. Analysis of the N-UNCD films revealed that N atoms are inserted in the grain boundaries and satisfy dangling C atoms bonds, providing electrons for electronic conductions. We will discuss the conductivity mechanisms in both B-UNCD and N-UNC films and their potential applications to a new generation of energy related and high power electronic devices.

9:45 AM ES07.04.06 Analysis and Ionic Conductivity of Lithium Carbonphosphonitride Thermosets Andrew Purdy$^1$, Brian L. Chaloux$^1$, William A. Maza$^2$, John A. Perry$^1$, Matthew G. Laneti$^1$, Kristi N. McPherson$^1$, Rachel E. Carter$^2$, Daniel M. Fragiadakis$^1$, Megan B. Sassim$^3$ and Albert Epstein$^1$; $^1$Naval Research Laboratory, Washington, District of Columbia, United States; $^2$NRC Postdoc at NRL, Washington, District of Columbia, United States; $^3$NREL Intern at NRL, Washington, District of Columbia, United States.
Lithium dicyanamide (Li[N(CN)]$_2$) reacts with phosphorus cyanide (P(CN)$_3$) in ethereal solution to form a resin, which separates into a second liquid phase, which is then redissolved in acetonitrile or other solvents. The resin can also be prepared in a single solvent in which it remains soluble for several days (pyridine), or indefinitely (propylene carbonate). The resin solution is used to coat metal coupons or disks which are then cured at temperatures of up to 300 °C, forming adherent, ion conducting films. Samples were also prepared in button cells. We characterized the ionic conductivity and chain motions of these films by dielectric relaxation spectroscopy, and the transference number by electrochemical measurements. Furthermore, bulk thermostet material was analyzed by elemental analysis. We evaluated how the composition and conductivities of these materials depend on conditions of preparation.

### 10:00 AM BREAK

#### 10:30 AM ES07.04.07

**Encapsulating Various Sulfur Allotropes within Graphene Nanocages for Long-Lasting Lithium Storage**  
Jun Lu  
Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois, United States.

The encapsulation of sulfur within carbon matrices is widely utilized in the cathode of a rechargeable lithium-sulfur battery, whose energy density largely depends on the design of the carbon structure. Here we report an advanced graphene nanocage structure with the capability of hosting both cyclo-S$_2$S and smaller sulfur molecules (S$_2$). The cage inner cavity is partially filled with S$_2$ to form a yolk-shell structure that enables free volumetric variation of S$_2$ during (de)lithiation. In the graphene shell of the cage, S$_2$ is downsized to S$_{2x}$ to activate extra sulfur loading sites within graphene layers. Importantly, the graphene shell exhibits inward volumetric variation upon (de)lithiation of the loaded S$_{2x}$, and the overall electrode strain is thus minimized. This prototyped design promises an ultimate solution to maximize sulfur loading in carbon matrices as well as to circumvent the polysulfide dissolution problem and boost the commercialization of lithium-sulfur batteries in the future.

#### 11:00 AM ES07.04.08

**Electrochemical Quartz Crystal Microbalance for Study of Iodide Affinity to Carbon Surface**  
Anetta Platek, Krzysztof Fic and Elżbieta Frackowiak; Poznan University of Technology, Poznan, Poland.

Nowadays iodides have been extensively used in electrochemical capacitors in order to boost their energy output. Due to the presence of relatively fast reaction of 2I$^-$/I$_2$, redox couple specific capacitance recorded on the positive electrode is extremely high. However, kinetics conditions of this process limit high rate ability of the system, what is its main drawback. Furthermore, other ambiguous issues could be listed as: low energetic efficiency of charging/discharging process at higher voltage range, iodide confinement only in the positive electrode responsible for electric double layer (EDL) creation, their exact movement and interactions with water molecules. For detailed studies, a rubidium iodide aqueous solution has been selected using EQCM. It has been revealed that iodide anions do not participate in EDL creation. During negative polarization movement of cations with solvation shell (Rb$^+$) have been described simultaneously with fluxes of H$^+$ and OH$^–$. Notwithstanding, for positive polarization mass change recorded is significantly smaller than it was expected for bare I$_2$. Therefore, recorded mass have been recalculated to exact species responsible for this phenomenon. It disclosures that OH$^–$ ions are equilibrating the charge in EDL during positive polarization. In order to clarify and confirm this phenomenon rubidium hydrioxide have been analysed. EQCM is capable to detect mass change resulting from OH$^–$ movement with satisfactory quality. Moreover, it has been revealed that cations and anions affect their solvation shell. For rubidium hydrioxide Rb$^+$ ion is hydrated with 2 molecules of water (Rb$^+$)$^{2+}$(H$_2$O)$_2$. Furthermore, sodium and potassium iodides have been analysed in order to verify versatility of iodide affinity to carbon surface. In all iodide solutions, a confinement of I$_2$ into porosity has been validated, as during positive polarization only OH$^–$ ions were responsible for charge balance. Solution number of alkali metals (Na$^+$, K$^+$, Rb$^+$) have been experimentally determined by this in-situ technique. Moreover, this work proves that ions adsorption/desorption in aqueous solution reveals very complex mechanism and description of ongoing processes cannot be simplified as long as solvent interaction with ions are considered. Iodide affinity to carbon surface have been clearly demonstrated by electrochemical quartz crystal microbalance.

#### 11:30 AM ES07.04.09

**The Electronic Structure Underlying Carbon for Energy Applications**  
Yuan Yue Liu; The University of Texas at Austin, Austin, Texas, United States.

The electronic structure theory (e.g. density functional theory) and calculations are powerful tools to offer mechanistic insights. Here I will discuss how the electronic structure of carbon controls atoms adsorption, and use this understanding to explain a number of puzzles related with energy applications, including: (1) why structurally similar C forms have distinct binding energies with Li$^+$ [1], (2) why graphite has a low Na capacity while a high capacity for other alkaline metals [2]. Finally, I will discuss the effects of varying charge and fixed potential in electrocatalysis of graphene [3], which are often neglected in modeling but are important for 2D materials due to their peculiar electronic structure, calling for re-evaluation of their electrocatalytic mechanisms by incorporating these effects into simulations.

2. Y. Liu, B. V. Merinov, W. A. Goddard, PNAS 2016, 113, 3735-3739  

#### 11:45 AM ES07.04.10

**Effect of Ionic Liquid Confinement in Carbon Nanopores on Electrical Double-Layer Charging**  
Vladimir Pavlenko, Emmanuel Pamete Yambou, Barbara Gorska and Francois Beguin; Poznan University of Technology, Poznan, Poland.

Room temperature ionic liquids (ILs) represent a perspective class of electrolytes for energy storage devices, particularly electrochemical capacitors (ECs). However, the relatively high melting point of ILs limits their applicability at low temperature, which is a requirement for commercial ECs. Accordingly, lowering the melting point of ILs down to -50°C, and even beyond, is a great challenge. The first strategy to expand the liquid state of IL electrolytes to sub-zero temperatures is the formulation of binary mixtures. Besides, since ECs are primarily constructed from porous carbon electrodes, and it was already proven that the IL melting temperature maybe depressed under confinement in porous silica, it is interesting to investigate if this effect also occur with carbons. Three aprotic ILs consisting of the same imidazolium-based cation (EMIm) and FSI, TFSi, BF$_4$ anions were selected for this study.

The thermal behavior and physico-chemical properties of EMImFSi, EMImTFSi, EMImBF$_4$, and their binary mixtures with various molar ratios were investigated. Some binary mixtures did not show any first order transition unlike the neat ILs, and remained in the liquid state down to -90°C, where only a glass transition was observed. The temperature dependence of dynamic viscosity and ionic conductivity for pure ILs and their mixtures followed the Vogel-Tammann-Fulcher equation, whilst the density showed a linear decrease. The corresponding Walden plot for pure ILs and their mixtures revealed a high degree of ionicity classifying them as “good ionic liquids”. Hence, by implementing BP2000 carbon (Cabot), carbon/carbon capacitors using binary mixtures (1:1 molar ratio) as electrolytes operated down to -40°C with good performance, contrary to the cells with the parent neat ionic liquids.

In a second part of the research, the effect of confinement in porous carbons – microporous carbon Maxsorb (Kensai) and mesoporous carbon Maxsorb (Cabot) with average pore sizes of 0.9 nm, 3.7 nm and 9.2 nm, respectively - on the phase transitions of neat ILs has been studied by differential scanning calorimetry. The SC2A (Cabot) with average pore sizes 0.9 nm, 3.7 nm and 9.2 nm, respectively - on the phase transitions of neat ILs has been studied by differential scanning calorimetry.

During (de)lithiation of the loaded S$_{2x}$, the intensity of the peaks corresponding to crystallization and subsequent melting decreased and the melting temperature downshifted to a value depending on the type of IL. For instance, as compared to the neat IL, the melting temperature of EMImTFSi confined in Maxsorb MSP-20X (for V$_{t}$/V$_{m}$=0.9) is downshifted by 6.5°C. Finally, for V$_{t}$/V$_{m}$> 1, we did not observe any freezing/melting peak, suggesting that freezing is prevented when ILs are such dispersed within the nanopores that they cannot form an ordered crystal structure. For V$_{t}$/V$_{m}$>1, it is also worth noting that the IL glass transition disappeared, whilst it still exists for the two mesoporous carbon matrices.
Raman spectroscopy is one of the most used characterization techniques in carbon science and technology. The measurement of the Raman spectrum of graphene triggered a huge effort to understand phonons, electron–phonon, magnetophonon and electron–electron interactions, as well as the influence of the number and orientation of layers, electric or magnetic fields, strain, doping, disorder, quality and types of edges, and functional groups. I will review the state of the art, future directions and open questions in Raman spectroscopy of graphene and carbon materials, focussing on the effect of disorder, doping, stress.

2:00 PM *ES07.05.02
Directional Flow-Aided Sonoechemistry Yields Graphene with Tunable Defects to Provide Fundamental Insight on Sodium Metal Plating Behavior

David Mitlin\(^1\)\(^2\) and Wei Liu\(^1\); 1Clarkson University, Potsdam, New York, United States; 2SCU, Chengdu, China.

We report a directional flow-aided sonoechemistry (FAS) exfoliation technique that allows for unparalleled control of graphene structural order and chemical uniformity. Depending on the orientation of the shockwave relative to the flow aligned graphite flakes, the resultant bilayer and trilayer graphene is nearly defect free (at-sonication graphene [AES-G]) or is highly defective (in-plane sonication graphene [IPS-G]). AES-G has a Raman G/D band intensity ratio of 14.3 and an APS derived O content of 1.3 at.%, while IPS-G has kossel of 1.6 and 6.2 at.%. AES-G and IPS-G are then employed to understand the role of carbon support structure and chemistry in Na metal plating/striping for sodium metal (SMB) anodes. The presence graphene defects and oxygen groups are highly deleterious: In a standard carbonate solution (1M NaClO\(_4\), 1:1 EC:DEC, 5vol.%/FEC), AES-G gives stable cycling at 2 mA/cm\(^2\) with 100% CE (within instrument accuracy), and an area capacity of 1 mA/cm\(^2\). Meanwhile IPS-G performs on-par with the baseline Cu support in terms of poor CE, severe mossy metal dendrites, and periodic electrical shorts. We argue that SEI stability is the key for stable cycling, with defects IPS-G being catalytical towards SEI formation. For IPS-G, the SEI layer also shows F-rich "hot spots" due to accelerated decomposition of FEC additive in localized regions.

2:30 PM BREAK

3:30 PM *ES07.05.03
Advanced Carbon Materials for Lithium-Sulfur Batteries—From Basic Research to Pouch Cells

Stefan Kaskel\(^1\); 2Fraunhofer IWS, Dresden, Germany; 3Chemistry, TU Dresden, Dresden, Germany.

Lithium sulfur batteries are considered as the next generation batteries due to their high gravimetric energy density up to 350-400 Wh/kg. Highly porous carbon materials with surface areas up to 3000 m\(^2\)/g play a key role for the performance of such systems. A key requirement is to achieve high sulfur loadings up to 75 wt. % in the cathode and high degree of sulfur utilization. In particular challenging is to identify new electrolytes to achieve high cycling stability. Electrolyte minimization is an often overlooked requirement to achieve high energy densities in prototype cells. The development of porous carbon materials for lithium sulfur batteries requires pore size and polymer tailoring [1-8] Mesoporous carbon materials are ideally suited as sulfur host for the lithium sulfur batteries. Microporous carbons (d < 2 nm) show high sulfur utilization but the overall sulfur loading is limited to a maximum of about 50 wt % sulfur posing limitations to achieve a high gravimetric energy density. Hard carbons are highly promising anode materials to achieve up to 4000 cycles in a lithium sulfur battery with only minor degradation.[3] Moreover, sodium sulfur batteries can operate with this concept at room temperature.[5] The presentation will give examples for pouch cell production, laser cutting, silicon anode integration [9] and fundamental advances for cathode evaluation [10].


4:00 PM ES07.05.04
Structure of Bulk and Confined Ionic Liquids from Ab Initio Molecular Dynamics Simulations and X-Ray Scattering

Tuan Anh Pham\(^1\), Riley Coulthurd\(^2\), Mirjam Zobel\(^3\), Steven Buchsbaum\(^1\), Destree Plata\(^1\), Brandon C. Wood\(^1\), Francesco Fornasiero\(^4\) and Eric R. Meshol\(^1\); 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3University Bayreuth, Bayreuth, Germany; 4Yale University, New Haven, Connecticut, United States.

Room temperature ionic liquids (ILs) have recently emerged as highly promising electrolytes for a wide range of emerging energy technologies, including next-generation supercapacitors and ion-batteries, due to their high thermal stability, ionic conductivity and wide electrochemical windows. In this presentation, we combine first-principles simulations and synchrotron X-ray characterization experiments to unravel the key structural properties of several imidazolium-based ILs. In particular, we use extensive ab initio molecular dynamics simulations to probe the local density distribution and medium-range order of bulk ILs, which can be directly compared and validated by X-ray scattering measurements. Having established this cross-validation, we then compare and contrast via simulation the structural, chemical and electronic properties of the ILs in the bulk and under confinement in sub-2 nm carbon slit nanopores, which serve as model systems for understanding confinement effects in porous carbon and eventually new carbon chemistry. Our integrated theoretical and experimental approach relates these structural and chemical signatures with the intrinsic cation-anion interactions, by considering bulk and under confinement in sub-2 nm carbon slit nanopores, which serve as model systems for understanding confinement effects in porous carbon and eventually new carbon chemistry. Our integrated theoretical and experimental approach relates these structural and chemical signatures with the intrinsic cation-anion interactions, by considering ILs with anions having significant differences in the molecular geometry, chemical composition, and charge distribution.

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

4:15 PM ES07.05.05

In Operando Characterization of SEI Formation and Long Term Cycling in NMC/SiGr Composite Pouch Cells Through Non-Invasive Acoustic Measurements

Clement Knebeler\(^1\); Jianlin Li\(^2\), Shaorui Biwas\(^1\); Jagjit Nanda\(^1\) and Daniel Steinberg\(^1\); 1Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; 2Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States; 3Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States; 4Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 5Feasible, Inc., Berkeley, California, United States.

Silicon/Carbon composite anodes for LIBs have been the subject of much research over the past decade, as they are touted to be the material that will enable the arrival, and commercialization, of the 'next-generation' LIB. That being said, there are many problems, ranging from the Si volume change, continuous SEI formation, and loss of Li-inventory in a full cell setting, have hindered its growth. Moreover, characterization of these processes to enable an understanding of structure-property relationships requires either destructive ex-situ methods, or labor and cost intensive in-situ, or in-operando methods, which can be out of reach for academic labs or early incubation start-ups. As such, this work attempts to develop a non-invasive understanding of degradation methods of a Si/Carbon composite in a full-cell, through a simple, non-destructive, and easily applicable in-operando acoustic characterization. Through the acoustic measurements, we are able to show a two step SEI formation process, involving a gassing, and non-gassing phase, as well as the gradual time-of-flight (TOF) increase due to the passivation of the Silicon in the full cell. Coupling these results with a comprehensive dq/dv, and half-cell
Probing Local Structure and Disorder in Graphitic Carbon Nitrides

Diane Haider, Barnaby D. Levin and Peter Czoor; Arizona State University, Tempe, Arizona, United States.

Graphitic carbon nitrides have emerged as promising candidates for driving photocatalytic H2 evolution under visible light, CO2 reduction, and other renewable energy applications owing to their native high surface area, chemical robustness, and inexpensive synthesis routes.1 Calculation of various N-rich precursors yields layered C3N4Hx compounds with interplanar spacings of ~0.32 nm. Although commonly referred to as “g-C3N4,” the average structure of these C3N4Hx’s are consistent with polymeric Melon (C3N4H) whose in-plane structure is composed of amine (N-H) bridged heptazine (C3N4) building blocks.2 In this view, the in-plane structure is polymerized through bridging N-H units to form “zigzag” chains of heptazine molecules terminated by N-H moieties. However, structural differences between different C3N4Hx compounds are not well understood as X-ray diffraction (XRD) and related techniques are limited to the bulk. High spatial resolution techniques, such as transmission electron microscopy (TEM), may be leveraged to investigate the in-plane structure/disorder in C3N4Hx compounds.

Here, aberration-corrected TEM at 300-kV under low dose rate conditions (<70 e/Å2/s), enabled by the use of a direct electron detector (K2-ES, Gatan), was applied to three C3N4Hx powders demonstrating a range in structural condensation. Prior to TEM imaging, the extent of long-range order in each sample was ranked based on the relative Bragg peak broadening observed in XRD patterns. For each sample, large field of view (~60-80 nm) images of the in-plane structure were obtained by imaging regions wherein the extended layers were perpendicular to the incident electron beam. Fourier transforms (FTs) generated from these “in-plane” images from each compound exhibit exceptional spatial resolution compared to that of XRD which is evidenced by the multiple (6θ°) reflections observed up to (1 Å)1 in the most ordered C3N4Hx. When rotationally-averaged FTs are compared to the XRD patterns, a similar trend in Bragg peak broadening is observed suggesting that the low dose rates used have avoided significant structural degradation.

To investigate local variations in the in-plane structure of each C3N4Hx, image autocorrelations were computed over 6.5-nm windows covering the entire field of view. Each autocorrelation represents a pseudo Patterson function (PPF), revealing the heptazine-heptazine nearest neighbor (NN) distances/orientations, associated with a particular region. The PPF analysis suggests that the local structure of the most ordered C3N4Hx is relatively invariant and possesses a “zigzag” chain structure. In contrast, the more disordered forms exhibit considerable rotational variations in the local hexagonally-coordinated NN motif. To visualize the extent of uniformly-oriented in-plane domains for each material, virtual dark field (VDF) images were generated from the same set of TEM images. VDF images of the most ordered C3N4Hx show “domains” covering tens of nanometers whereas in the disordered forms, these domains are much smaller at ~2-7 nm at most.


Preparation of Nitrogen-Doped and Interconnected Hollow Carbon Nanospheres for Superior Lithium-Sulfur Battery

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Sulfur is the promising cathode materials for rechargeable lithium batteries with high theoretical specific capacity and energy density. However, sulfur has poor cycling stability due to its low conductivity and polysulfide dissolution. Herein, nitrogen-doped and interconnected hollow carbon nanospheres with particle size of 50-80 nm via direct carbonization of Zn, Co-ZIF coated with resorcinol-melamine-formaldehyde resin have been reported as highly efficient sulfur host for high-performance lithium-sulfur batteries. The interconnected hollow nanospheres are derived from the different carbon yield and shrinkage between Zn, Co-ZIF core and RMFs shell and the as-prepared HPCNs have the specific surface area of 836-881 m2/g, large pore volume up to 1.50 cm3/g and high conductivity. Combining the high conductivity and chemical trapping of lithium polysulfides, the obtained S/HPCNs cathode of 70 wt.% sulfur content in the composite delivered a high specific capacity up to 1300 mAh/g at 0.2 C and 762 mAh/g at 8 C. Moreover, a stable capacity of 950 mAh/g could be maintained even after 200 cycles at 0.2 C. The nature of the interactions between N-doped carbons and lithium polysulfide species was investigated by X-ray photoelectron spectroscopy studies. The unique electrochemical behavior and superior performance of S/HPCN composites open possibilities for new class of cathode materials for high energy and high power density lithium rechargeable batteries.

Surface Functionalization of Graphene Prior to Co2+: Tethering for Oxygen Reduction Catalysis in Both Acidic and Alkaline Media

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Oxygen reduction reaction (ORR) is one of the most studied reactions for clean energy devices such as fuel cells and metal-air batteries due to its intrinsically sluggish kinetics.
which often limits device performance. Non-precious transmission metal oxides (TMO) such as FeO,
MnO, and CoO[1] have been intensively probed as alternatives to platinum-based catalysts. To supplement low electronic conductivity of TMOs, they are often dispersed on a highly conductive carbon nanostructure with a large surface area, maximizing catalytically active sites per volume and mass.

We employ a hybrid structure where CeO2 is deposited/decorated on reduced graphene oxide with extreme surface area and excellent electronic conductivity. Since only the wrinkles and edges contain active sites (binding functional groups) on graphene oxide, the basal plane is populated with rather inert epoxide groups. To functionalize the GO surface, hydrobromic and/or oxalic acids are used to create hydroxyl or carboxyl groups. The treated GO is then hydrothermally reacted (at 160 °C for 24 h) with the precursor salt of cerium (III) nitrate hexahydrate. Three different kinds of GO:CeO2 hybrids were synthesized based on as-synthesized, hydrobromic acid-treated, and an additional oxalic acid-treated GOs.

Results have indicated that hydroxyl groups absorb CeO2 nanoparticles better and that CeO2 tethered on hydroxylated GO showed the best performance in acidic media in terms of current density, electron transfer number and onset/half-wave potential, all comparable to the performance of Pt/C. Similar enhanced performance was seen for alkaline media with an exception of enhanced durability compared to Pt/C. An X-ray analysis showed a reoccurring (002) diffraction peak among most hybrids with the exception of hydroxylated CeO2/GO hybrids. This suggests the sample exhibit a strong binding of metal oxides to the basal planes of graphene flakes, thus prohibiting graphene restacking. From a series of experimental analyses, it is concluded that a strong tethering of metal oxide particles on the basal plane of graphene is a prerequisite of high ORR performance, and that the particle-graphene interfaces (as opposed to the particle or graphene itself) dictates the performance and reaction route.

This project was funded by NASA Advanced STEM Training and Research (ASTAR) Fellowship.

References:

ES07.06.03

The Effect of Synthesis Parameters for the Mesoporous Carbons Using Silica Aerogel Templates

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Hydrogen is considered as one of the most promising future energy carrier due to its high energy density and its production through ethanol steam reforming reaction (SRE) has the potential to be used for its on board production, in fuel cell powered motor vehicles. Nowadays, novel catalysts are investigated for the steam reforming of ethanol reactions in order to achieve high hydrogen yield with low coke formation. One of the novel catalyst is a mesoporous material templated mesoporous carbon. Mesoporous carbon materials are investigated due to their physical and chemical properties, such as electrical and thermal conductivity, mechanical and chemical stability, low density, high surface area, and large pore size. Using the mesoporous materials such as SBA-15, MCM-48 etc. as a template, having a high surface area and pore diameter carbon supports can be synthesized.

Generally, hard template method is used to achieve well-defined ordered structure. Saccharic and furfuryl alcohol are used as carbon precursors and for the removal of silica materials, washing with HF or NaOH are applied. In this study, for the first time, silica aerogel was used as silica template. Moreover, sucrose was impregnated to the pores of the mesoporous materials as a carbon precursor. The effect of washing with HF or NaOH, adding silylating agent to silica aerogel in the synthesis and calcination temperature of silica aerogel on the structure of the materials were investigated. The results showed that high surface area materials with Type IV isotherm were synthesized. The carbon materials washed with HF gave higher surface areas compared to the materials washed with NaOH. It was evident that NaOH did not remove the all silica materials. The result also proved with the SEM and EDS analysis, showing the unremoved silica structures in the materials. In addition, washing with HF resulted in highly acidic carbon materials considering TPD analysis. When the silica aerogels which did not contain silylating agent as a template, the final carbon materials gave high surface area and pore diameter. Moreover, the calcination temperature of the silica aerogels did not affect the surface area and pore diameter of the carbon materials. The nickel was impregnated into these materials and they were tested in the steam reforming of ethanol reaction. The carbon material washed with HF suppressed the ethanol steam reforming reaction and favored the ethanol decomposition reaction, giving undesired products CH4 and CO. The hydrogen yield was 3.8 using the carbon material washed with NaOH as a catalyst.

ES07.06.04

Multiscale Simulations of Hole Formation and Growth During Holey Graphene Synthesis via Chemical Etching

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Holey graphene is a derivative of graphene that has abundant nano-holes on the basal plane of graphene sheets and has shown great potential in electrochemical and biochemical applications. Currently, the most popular synthesis method for holey graphene is the chemical etching approach, during which the mixture of graphene oxide and hydrogen peroxide are heated to generate holey graphene. However, the fundamental mechanism for the hole formation and growth during synthesis has not been fully revealed. To address this problem, this study employs density functional theory simulation to analyze and compare the various reactions between graphene and hydrogen peroxide. Molecular dynamics simulation are carried out to discuss the kinetics of the hole formation and growth. Results show that the carbon atoms around the defect areas on graphene sheets can be removed under high local temperature leaving baby holes on the basal plane. The presence of both hydrogen peroxide and high temperature ensures the cyclic insertion and removal of functional groups around those baby holes, which eventually causes the continuous growth of the in-plane holes.

ES07.06.05

Pillared Reduced Graphene Oxide with Mg in the Interlayer Space as Hydrogen Storage Material

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Hydrogen is a promising sustainable alternative to conventional fuels that can push forward the energy transition. The caveat of this technology is the storage, since gravimetric and volumetric density targets have proven hard to reach. Theoretical studies of the gravimetric densities on graphene and in magnesium predict 8.3 wt% and 7.6 wt%, respectively. However, these values are still far from reality because of the weak physisorption and high chemisorption temperature. Herein, a novel pillared reduced graphene oxide with Mg in the interlayer space is proposed for effective hydrogen storage. The material, realized by sol-gel reaction of an organosilicon precursor, was characterized with BET, SEM, XPS, XRD and TEM and shows a crosslinked mesoporous structure with high specific surface area, narrow interlayer distance and enhanced adsorption due to the alkaline hydrides.

ES07.06.06

Influence of Carbon Microstructure on High-Performance Supercapacitor

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Transport porosity in activated carbon microstructure plays a key role in determining the electrode performance in electrochemical capacitors. In particular, ultramicropores and mesopores can significantly contribute to the charge storage properties in ionic liquid-based EDLCs. We designed and evaluated several carbons derived from polymer precursors with distinct pore texture that exhibit bimodal porosity in order to study and compare the effect of transport pores to the ionic liquid-based EDLC performance. This work provided insight into the synergistic influence of pore size distribution in determining the energy, power, voltage, thermal stability and lifetime of the electrochemical capacitor. The performance of the devices was evaluated using several techniques including floating voltage test, 3-electrode measurements, impedance spectroscopy, and constant current charge-discharge test. In this study, we demonstrated excellent voltage stability and good capacitance retention >90% for bimodal carbons with operating voltage up to 3.8 V.

In addition, the aforementioned activated carbon materials were used as the cathodes materials to fabricate Lithium-ion capacitors. In particular, bimodal activated carbon cathode in conjunction with intercrossed carbon onion anodes shows excellent power and energy density. Hence, we were able to fabricate a capacitor with energy and power density of 52 Wh/kg at 7.3 kW/kg, respectively. The device showed outstanding capacitance retention of 80% after 21000 cycles and remarkable energy efficiency of >90%. Additionally, the temperature stability of the device was tested ranging from room temperature to 60°C.

ES07.06.08
Performance Recovery in Degraded Carbon-Based Electrodes for Capacitive Deionization

Ion batteries, as promising energy storage device have been widely used in portable electronics, power tools, and electric vehicles due to their high electrochemical potential, superior energy density and long cycle life. Considering the relatively high theoretical capacity (170 mAh g⁻¹), cost effectiveness, long cycle life, good thermal stability, and environmental friendliness, lithium iron phosphate (LiFePO₄, LFP) has been demonstrated as a suitable cathode material for LIBs. However, key limitations of LFP are its low intrinsic electronic conductivity (10⁻¹⁰ to 10⁻¹⁴ S cm⁻¹) and limited lithium ion diffusion channel, leading to poor rate capabilities in LFP batteries. To overcome the drawbacks of LFP, an effective way to increase conductivity is combining LFP with conductive materials. Carbon-based materials such as graphite, carbon black, graphene, and carbon nanotubes are one of the best conductive materials for LFP. Especially, carbon quantum dots (CQDs), a new type of carbon-based material, are also of high interest due to their high surface area, low toxicity, cost-effectiveness, and controllable size. However, CQDs contain a high amount of sp³ carbon, resulting in low conductivity. In this work, we investigate high-quality graphitic CQDs with diameters below 10 nm for improving the conductivity of LFP. CQDs can play a key role in energy storage for improving the electrical conductivity and charge transfer reactions in LFP batteries, since increasing the ratio of sp² to sp³ carbon exhibits better electronic conductivity, resulting in enhanced battery performance. We report the synthesis of CQDs by a hydrothermal method at different reaction temperatures (160°C to 200°C) and times (60 min to 180 min) from organic materials. High-quality graphitic CQDs are produced by using a dehydrogenation reaction. The morphology and size distribution of CQDs were characterized by transmission electron microscopy (TEM). The chemical bonding states and sp³/sp² ratio of synthesized CQDs were characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

SESSION ES07.07: Carbon-Based Materials for Supercapacitors and Batteries

Performance Recovery in Degraded Carbon-Based Electrodes for Capacitive Deionization

Li and Steven T. Boles; The Hong Kong Polytechnic University, Hong Kong, China.

Limitations of capacitive deionization (CDI) technology and future commercialization efforts are intrinsically bound to electrode stability. In this work, novel regeneration methods are explored which mitigate previously explored degradation mechanisms. Electrode-exchange studies indicate that only the anode undergoes degradation over cycling, during which both the physical and chemical properties change evidently. In particular, acidic functional groups, which are derived from the reported oxygen-containing functional groups, are formed in the anode during cycling and these account for the potential of zero charge (PZC) change of the anode, thereby degrading the overall performance of the cell. Annealing treatment of aged electrodes suggests that low temperature thermal treatments can recover the degraded properties of anode and therefore regenerate the performance of the CDI cell. Thus, the lifetime of electrode can be prolonged by applying intermittent annealing treatments once the severe degradation becomes observable. The regeneration mechanism studies also offer insights into strategies for minimizing electrode degradation or in-situ regeneration as the technology gains momentum for future commercialization.

Asymmetric Flasklike/Bowl-Shaped Carbonaceous Nanoparticles Fabricated by the Synergistic Interaction Between Soft Template and Biomass

Chun H. Chen and Yong Wang; Zhejiang University, Hangzhou, China.

In the past two decades, an expanding library of new nanoparticiles have been developed, among which anisotropic ones, such as concave, janus, and patchy particles, have gained substantial focus due to their high complexity and nanoscale anisotropy in structure. These novel patterned nanoparticles may have possibly new or enhanced traits, and therefore could be highly desirable in both fundamental studies and potential applications in various fields, such as photonics, biomedical applications and building blocks for advanced materials and functional nanodevices.

In addition, most of the asymmetric hollow nanoparticles reported are limited to silica, polymer latex (e.g., polystyrene), or metal oxides, whose synthetic routes are lengthy and typically involve toxic organic polymers or caustic reagents. Because of the advantages of large voids, good biocompatibility, chemical inertness, and high conductivity, hollow-structured carbonaceous materials have been extensively investigated. However, they are mostly spherical in shape. Thus, preparing asymmetric carbonaceous structures remains a great challenge.

The soft template method is broadly applied to the fabrication of hollow-structured nanomaterials. However, due to the instability and the typical spherical shape of these soft templates, the resultant particles have a spherical morphology with a wide size distribution. Herein, we developed a sustainable route to fabricate asymmetric carbonaceous structures with a highly uniform morphology and a narrow size distribution using the soft template method.

The synthetic method can be further classified into two main categories: in-situ polymerization of precursors process forms the anisotropic structures and the ex-situ process such as post-treatment induces the anisotropy.

Scalable Pore Size Tuning Process for Seeking Better Cathode of Lithium-Ion Capacitor and Development of High-Performance Full Cell Device Through It

Jong Ho Won and Jeong Ku Kang; Applied Science Research Institute, Korea Advanced Institute of Science and Technology, Deajeon, Korea (the Republic of); Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Deajeon, Korea (the Republic of).

With the development of the industry, the need for better energy storage devices that can be used in various devices continues to grow, but the pace at which practical alternatives are developed is very slow. Many prior studies have succeeded in increasing the energy density of lithium-ion batteries to a significant level, but they have not been able to lead to actual production due to battery instability, life problems, production and price issues. Many battery manufacturers currently faced the limit capacity of the cathode and are aiming to improve the energy density by developing an energy density of 430 mAh/g by mixing graphite with a high capacity active materials. However, in such a method, it is difficult to satisfy the high power density due to the difference in charge/discharge speed between the graphite and the high capacity active material. So, in reality, current access and pricing policies are not able to create a significant gap in the lithium ion battery platform. For this reason, the study of lithium-ion capacitors satisfying both energy density and power density has received much attention due to its high versatility. Lithium-ion capacitors can use conventional lithium-ion anodes and use carbon materials instead of heavy metal alloys as cathodes. Initial lithium-ion capacitor research was concentrated on an anode capable of high capacity such as a lithium-ion battery. In fact, the main factor that determines the capacity per mass/volume of lithium-ion capacitors is the capacity of the cathode. As the cathode of the lithium-ion capacitor, a porous carbon material which has been used as the electrode material of the electric double layer capacitor has been widely used. However, the electrode of the EDLC stores OH- ions, while the cathode of the...
lithium-ion capacitor should adsorb and store much larger ions such as PF6- ions. Thus, the electrode material originally used in the EDLC may be unsuitable for storing larger ions due to the small pore size. Here we have found improvements that can improve the capacity of lithium-ion capacitors. We intend to develop a cathode material for lithium-ion capacitors that can store larger ions such as PF6- ions in this work. We have developed seven cathode materials that composed of concentrate pores with a certain size using graphene and a template that is vaporized below 100 degrees of Celsius. The size of the pores ranges from less than 5 nm to 150 nm. Although the effects of the number of Angstrom pores have been addressed in the meantime, the impact of macro size pores has not been addressed in the lithium-ion capacitor research. We evaluated the capacity and characteristics of the developed cathode using PF6-, TFSI-, BF4-, CIO4-, and so on. In the experimental results, we confirmed that macro-sized pores have a profound effect on the adsorption and storage of ions and their obvious tendency. To put it briefly, the TFSI- and PF6- ions are significantly different in size, and thus the cathode with the highest capacity is different from each other, which is revealed by the tendency. Additionally, the full cell lithium-ion capacitor with developed cathodes and a commercial MCMB anode recorded the highest energy density of up to 145 Wh/kg and an energy density over 70 Wh/kg at a power density of 7200 W/kg. We have demonstrated the effect of macro-sized pores on the cathode of a lithium-ion capacitor and succeeded in developing a cathode material for an excellent lithium ion capacitor.

9:00 AM ES07.07.04
Laser Ablation and Laser Doping of Natural Carbonaceous for Electronics
Ximing Zang, Sam Iengsgoll, Nicolra Ferralis and Jeffrey C. Grossman; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recycling natural carbonaceous feedstocks for alternative applications beyond burning would provide new opportunities for these materials. For example, new technologies using coal or coal-derived byproducts such as tar could be engineered to produce thin films for electronics with highly tunable electronic properties. In this work, we illustrate how laser ablation can be used to develop alternative applications for natural carbonaceous materials (coal, tar, pitch) in order to tailor their electronic, magnetic, and optical behavior. This approach enables the use of carbonaceous feedstocks in variety of applications at extremely low cost (i.e. coal at 0.05$/kg, tar at a negative cost). We will present recent work on applications ranging from transparent heater, transistors, and flexible/stretchable electrodes. Furthermore, the laser process can also be integrated into large scale, continuous manufacturing techniques.

9:15 AM ES07.07.05
Geometrically Controlled Nanofibrous Carbon for Functional Devices
Steven Knau, Samuel Brennan and Mark Atwater; Millersville University, Millersville, Pennsylvania, United States.

One of the most significant challenges in developing nanoscale carbon devices is efficiently and precisely producing the carbon. Two recent developments make this possible with carbon nanofibers. The first is a fast, low-cost method of producing carbon for catalyst deposition. A nontraditional processing route of mechanical alloying is used to produce unique catalytic materials that exhibit enhanced kinetics. The second advancement is the ability to create integrated devices in situ. This allows carbon nanofibers to be created in specifically designed geometries with controllable properties. These nanowoven structures can be made with densities as low as aerogels or much higher, allowing the fiber spacing to be varied and a high surface area to be compact and flexible. Carbon nanofibers have been proposed for applications ranging from supercapacitors to hydrogen storage to filtration. Multiscale control has been demonstrated by producing free-standing structures centimeters in scale, and carbon nanofibers have been integrated with traditional carbon materials to create unique hybrids. The methods and capabilities, as well as key device applications, are highlighted.

9:30 AM ES07.07.06
Highly Capacitative Activated Carbon Fiber Clothes for Wide-Voltage (2 V) High-Energy-Density Aqueous Symmetric Supercapacitors
Kwadwo A. Owusu and Liqiang Mai; Wuhan University of Technology, Wuhan, China.

Carbon aqueous symmetric supercapacitors are attractive supercapacitor devices owing to the low-cost and high conductivity of porous carbons. However, the limited capacitive charge storage process in carbon symmetric capacitors in comparison to pseudocapacitors or asymmetric supercapacitors severely limit the energy density. The only effective strategy to enhance the energy density of carbon aqueous symmetric supercapacitor is to extend the cell voltage beyond the thermodynamic stability of aqueous electrolytes (1.23 V).

Also, in recent studies, researchers have focused on preparing high-performance carbon electrodes from commercial carbon fiber clothes by activating the surface usually through chemical and electrochemical routes. However, it is still a major challenge to realize a comprehensive electrochemical performance of high capacitances, excellent rate capability, stability and wide operational potential windows in the activated carbon fiber clothes.

Herein, we successfully activated the surface of commercial carbon fiber clothes using a facile-one-step air calcination at 400 °C for 6 hours strategy to realize a remarkable improvement in the surface area, porosity, and electrochemical performance. The successful activation of carbon fiber clothes is fully confirmed through BET tests, SEM, TEM, Raman and contact angle measurement tests. Specifically, the activated carbon exhibits a 450-fold increase in specific surface area (615 m2/g) which can be of benefit to commercial devices.

References:
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9:45 AM ES07.07.07
Capacitance of Functionalized Carbon Powders in Monolayer and Macroscopic Ultracapacitor Electrode Configurations
Steven R. D'Souza; and Jingue Liu; 1 Materials Science and Engineering, Arizona State University, Tempe, Arizona, United States; 2Physics, Arizona State University, Tempe, Arizona, United States.

Ultracapacitors, due to their high specific power, long cycle life, and ability to bridge the power/energy gap between conventional capacitors and batteries/fuel cells, have attracted considerable attention for commercial applications such as plug-in hybrid electrical vehicles. Functionalization of activated carbon powders with oxygen and nitrogen redox-active functional groups plays a dual role in (i) incorporating pseudocapacitance along with double-layer capacitance and (ii) providing anchoring points for further incorporation of stable metal/metal oxide nanoparticles to improve the energy density of the ultracapacitors of interest. We report here the sequentially doped commercial scale, microporous activated carbon (AC) with various amounts of oxygen and nitrogen moieties, and fabrication of the functionalized AC into monolayer and macroscopic (5 μm and 100 μm thick respectively) carbon powder electrodes structures. A comparison of electrochemical performance metrics in acidic and alkaline electrolyte indicates that the monolayer electrode configuration yields a significantly enhanced capacitance (250 F/g) than that of the macroscopic electrode (135 F/g), primarily due to increased accessible specific surface area, reduced diffusion length of the electrolyte molecules and reduction of contact resistance. While the behavior of pseudocapacitance and double-layer capacitance was clearly manifested in the monolayer electrode configuration, the macroscopic electrode configuration did not display these characteristics, presumably due to a large potential gradient. We have demonstrated that the capacitance of AC based ultracapacitors can be significantly enhanced by incorporating functional groups within the interior pores of the AC powders, which can be of benefit to commercial devices.

10:00 AM BREAK
All-solid-state batteries (ASSBs) with ceramic-based solid-state electrolytes (SSEs) and lithium metal anode enable high safety and high energy density that are inaccessible with conventional lithium-ion batteries. However, the large interfacial resistance between Li and SSEs has significantly hindered the development of ASSBs. Take Li/garnet SSE system as an example, garnet presents “lithiophobic” surface and poor contact with Li metal anode. To date, several groups have proved that coating a layer of “lithiophilic” material on garnet can improve the Li/garnet contact by the interfacial reaction. Here, we report a new strategy to solve the interface problem by adding carbonaceous materials into Li metal. The lithium-carbon (Li-C) composite shows dramatic change in wettability with garnet due the increased viscosity. The carbon can be graphite, carbon nanotube, graphene or their mixture. An intimate Li-C/garnet interface have been demonstrated and delivered a much smaller interfacial resistance compare to pure Li/garnet.

11:00 AM ES07.07.09
Design of Nanohybrid Materials to Enable Efficient Junctions for Strong Electrolyte Binding in Ionic Liquid-Based Supercapacitors Feili Lai, Martin Oschatz and Markus Antonietti; Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

Due to the temporal, fluctuating character of sustainable energy and the increasing use of rechargeable electronic devices, there is an urgent need for the development of more efficient electrochemical energy storage technologies. Electrical double-layer capacitors (also known as supercapacitors) have become attractive due to their rapid charge-discharge rate, high power density, long lifetimes, remarkably low price base, and potential sustainability of the involved materials. The use of ionic liquids (ILs) as electrolytes with a wide electrochemical stability window is the most promising strategy to improve the poor energy density of supercapacitors but the actual energy storage mechanism in absence of a solvent in the electrolyte remains poorly understood. Charge storage in a compression double-layer is not possible in ILs and thus new energy storage terms such as order-disorder transitions or solvation-desolvation processes likely play a rather important role. It will be shown that strong metal oxide-support interaction is crucial to activate high energy storage modes of carbon-supported hybrid electrodes in IL-based supercapacitors.

11:15 AM ES07.07.10
Designed N/O/S Tri-Doped Carbons for CO$_2$ Capture and Supercapacitors Zhihong Tian$^1$,$^2$, Feili Lai$^2$, Martin Oschatz$^2$, Shaokui Cao$^2$ and Markus Antonietti$^2$; $^1$School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, China; $^2$Colloids Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.

Porous functional carbons stand out for their special physical and chemical properties, including high chemical stability, large surface area, high porosity and good conductivity, and have been regarded as the most promising candidates for gas separation, energy storage and electrocatalysis. Recently, one sees rising attention for the development of designer carbons with controlled structure and local material composition, due to this enormous potential in practical application. However, it is still difficult to achieve preconceived carbon structures, which is ascribed to the irregular nature of current synthetic methods. Consequently, we strongly need approaches to circumvent this limitation, in which one possible way is to use the suitable precursors with “encoded information”. Here we present a new class of well-defined C$_{10}$N$_2$S$_2$ carbons that have both high content of N/O/S heteroatoms and large specific surface area (up to 1704 m$^2$ g$^{-1}$), which can be efficiently synthesized by the simple condensation using gallic acid and thiourea as the building blocks. To be noted, as a multi-functionally inexpensive natural chemical, gallic acid is well known to decarboxylate into pyrogallol at higher temperatures, so that the carboxylic acid unit can be regarded as a “protecting/leaving group” that enables a controlled substitution chemistry to realize the high structural definition. In this synthesis, thiourea is the direct source for both nitrogen and sulphur after decomposing at 180 $^\circ$C.

11:30 AM ES07.07.11
Improving the Performance of Lignin-Derived Supercapacitor Electrode by Inducing Lignin Crosslinking and Controlling its Derived Carbon’s Morphology Hoi Chun Hu$^{1,2}$, Ngoc Nguyen$^1$ and Amit Naskar$^1$; $^1$Oak Ridge National Lab, Oak Ridge, Tennessee, United States; $^2$The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Supercapacitor, a promising energy storage solution of the future, can meet the demand for our escalating energy storage needs for electric vehicles and the implementation of renewable energy. However, high cost and low energy density are preventing its wider adoption.

Within a supercapacitor device, the carbon electrodes are the costliest material, contributing up to half of a device’s raw material cost. Efforts in finding an alternative supercapacitor electrode carbon are needed to minimize its cost. Lignin, an underutilized renewable industrial waste and a major component in plants, can be the alternative supercapacitor electrode carbon precursor. It has been estimated that 50 million tons of lignin are produced annually in the US just from the paper and pulp industry alone. Because of lignin’s structural complexity and hyperbranching nature, researchers struggle to design lignin-derived carbon with a controllable morphology. Currently, lignin is mostly burned for heat and electricity.

In this study, we utilized the abundant thermal sensitive linkages present on lignin. By fine-tuning their crosslinking via a simple thermal stabilization step in air along with a 10% acrylonitrile-butadiene rubber (NBR) dope, the derived carbon’s porosity and morphology can be controlled. Because a supercapacitor’s performance directly correlates to the electrode carbon’s porosity, when made into supercapacitor electrode, the resulting lignin-derived carbon capacitance can be improved.

The increased degree of lignin and NBR-doped lignin crosslinking was first revealed from differential scanning calorimetry and thermogravimetric analysis by their thermal stability. After a one-step carbonization and chemical activation with potassium hydroxide, we found that NBR doping prior to carbonization and activation-induced macroporosity of the carbon. When porosity was further studied with nitrogen adsorption-desorption experiments, it was revealed that NBR doping improved lignin-derived carbon from 1750 m$^2$ g$^{-1}$ to 2120 m$^2$ g$^{-1}$ due to NBR templating. Thermal stabilization in air, however, reduced carbon’s surface area to 1585 m$^2$ g$^{-1}$. We hypothesized the drop was due to the change in lignin’s molecular weight and the shrinkage force induced from the additional crosslinking.

When the lignin-derived carbon was made into supercapacitor electrodes, as expected from the improved porosity, NBR doping improved lignin-derived carbon’s capacitance from 175 F g$^{-1}$ to 215 F g$^{-1}$. On the contrary, thermally stabilized lignin displayed a reduction of capacitance to 154 F g$^{-1}$. The best performing NBR-doped lignin-derived carbon electrode was then further tested with its long-term capacitance cyclability by cycling for 5000 cycles and showed an impressive 100% capacitance retention, suggesting a desirable electrochemical reversibility and stability. The 22% improvement in lignin-derived carbon’s porosity and capacitance demonstrated the feasibility of using simple NBR doping of lignin for an alternative supercapacitor electrode carbon source.
Graphite dual-ion batteries represent a potential battery concept for large-scale stationary storage of electricity, especially when constructed free of lithium and other chemical elements with limited natural reserves. Owing to their non-rocking-chair operation mechanism, however, the practical deployment of graphite dual-ion batteries is inherently limited by the need for large quantities of electrolyte solutions as reservoirs of all ions that are needed for complete charge and discharge of the electrodes. In this work, we will provide a balanced analysis of the overall cell-level energy density of graphite dual-ion batteries as a function of electrolyte concentration and cathodic capacity of graphite. We will discuss also other issues associated with this technology, one being the low oxidative stability of most metallic current collectors at high potentials of 4.5-5 V vs. Li+/Li. Finally, we will present a novel lithium-free graphite dual-ion battery utilizing a highly concentrated electrolyte solution of 5 M potassium bis(3-fluorosulfonyl)imide in alkyl carbonates. The resultant battery offers an energy density of 207 Wh kg\(^{-1}\), along with a high energy efficiency of 89% and an average discharge voltage of 4.7 V.

References


SESSION ES07.08: Carbon-Based Materials in Batteries

Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 127 A

1:30 PM *ES07.08.01

On the Role of Heteroatom Doping of Carbon-Based Catalysts for Water Splitting Reactions and the Oxygen Reduction Reaction
Ulrike Kramm, Ali Shahraei, Natalsha Weidler and Markus Kübler; Catalysts and Electrocatlysts, Department of Materials and Earth Sciences and Department of Chemistry, TU Darmstadt, Darmstadt, Germany.

Carbon-based catalysts play an important role in energy conversion devices such as fuel cells, metal air batteries and electrolysers. The group of Me-N-C catalysts (with molecular MeN\(_2\) sites) is formed by a high-temperature pyrolysis of metal, nitrogen and carbon precursors. Sulfur addition can be used to increase the density of MeN\(_2\) sites [1-3]. But sulfide species might also play an important role as active sites for some catalytic reactions, as shown for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

In addition to this, in our recent work we showed that the integration of carboxylic groups in close vicinity to active sites can be used to tune the catalytic activity [4-5]. In this work, we will present different strategies of multi heteroatom doping for tuning the OER activity and stability of cobalt-based catalysts [6] as well as ORR activity and selectivity of Me-N-C catalysts. It will be shown that with the integration of dopants all three parameters, namely activity, selectivity and stability, can be tuned to optimize the catalysts for the desired applications.

References


2:00 PM *ES07.08.02

Disordered Carbon Anodes for Na-Ion Battery and Their Sodium Storage Mechanism
Yaxiang Lu, Yunming Li, Chenglong Zhao, Yuheng Zheng, Xingguo Qi, Xiaohui Rong, Hong Li, Xuejie Huang, Liquan Chen and Yong-Sheng Hu; Key Laboratory for Renewable Energy, Institute of Physics, Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing, China.

Na-ion batteries have been recently reconsidered for storing the electricity from renewable energy due to the abundant sodium resources and low cost. Furthermore, we can use Na\(^+\) ions as the charge carrier to explore new chemistry and new materials to further decrease the cost. For example, Na cannot form the alloy with Al, therefore Al foil can be used as the current collector for the anode without the overdischarge problem. Among all available anode candidates, disordered carbon still shows the best overall performance in terms of capacity, cycling stability and cost. In this talk, I will present several superior low cost disordered carbon anodes made from pitch, renewable biomass and coal. In particular, some carbon exhibits Na storage capacity of 400 mAh/g with a high Coulombic efficiency. I will also discuss their Na storage mechanism. Then, prototype Na-ion pouch cells will be presented. Finally, the first mini-electric vehicle powered by Na-ion batteries was demonstrated in the world.

References


2:30 PM *ES07.08.03

Dual-Functional, Tunable, Nitrogen-Doped Carbon for High Performance Li-S Full Cell
Hongli Zhu; Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States.

Due to the high energy density and abundance of sulfur, lithium-sulfur (Li-S) batteries are attracting broad interest. However, several hurdles need to be tackled before commercialization. For example, the batteries experience the polysulfide shuttle effect in cathode and dendrite growth in the lithium metal anode. Herein, for the first time, a mesoporous carbon sphere (MCS) that simultaneously boosts the performance of the sulfur cathode and the metallic lithium anode was designed in this work. The MCS homogenizes the flux of lithium ions and inhibits the growth of lithium dendrites, due to its high-surface-area honeycomb structure and abundance of nitrogen sites. Upon covering multiple mesoporous carbon spheres (CMCS) with a layer of amorphous carbon, individual carbon cage encapsulated sulfured inside. This reduced the polysulfide shuttle, which improved the cycle-stability of the Li-S battery. As a result, the Li@MCS cell exhibited a small overpotential of 29 mV and long lifespan of 350 h under the current density of 1 mA cm\(^{-2}\) for the cycling performance. Meanwhile, the Sci@CMCS maintained 200 cycles from the capacities of 411 mAh g\(^{-1}\) to 400 mAh g\(^{-1}\) at a current density of 2 C (3350 mA
H. Tabassum, Asif Mahmood, approach for the implementation and the development of a new bottom-up technique for hierarchical hybrid nanostructured electrodes based on vertically aligned carbon nanotubes (CNTs) composite has attracted considerable attention due to LTC’s high reversible capacity and physical and chemical merits of CNTs, which supplement LTC’s structural instability and low electrical conductivity. Despite the recent advances in LTC-CNT electrodes, there are still remaining critical issues limiting commercialization. The most difficult one is controlling the state of CNTs in LTC since the aggregation of CNTs resulted in undesirable structure and increased electrical resistance. These aggregated CNTs also lower the surface coverage of CNTs within the LTC, interrupting the electrons on CNTs to meet ions in the LTC and consequently decreasing the accessible redox sites. Therefore it is essential to control the aggregation of CNTs in materials to fully utilize the merits of CNTs and guarantee the accessible redox sites, which is denoted as maximizing “triple junction” where ions and electrons meet, suggesting that the origin of the high electrochemical performance is the perfect harmony of ion, electron, and redox sites together.

Herein, N-doped hierarchical porous carbon with highly aligned CNTs was prepared by co-polymer single nozzle electrosprining, carbonization, and KOH activation. Densely and uniaxially packed CNTs not only improve the electrical conductivity but also act as a structural scaffold, enhancing electrochemical performance of the anode. A partially graphitized N-doped LTC shell was designed to expand the redox sites from the surface of the material to the whole material by having a rapid ion accessible pore network and abundant redox sites. This material exhibited a superior reversible capacity of 1814.3 mAh g\(^{-1}\) at 50 mA g\(^{-1}\) and 850.1 mAh g\(^{-1}\) at 1000 mA g\(^{-1}\). Furthermore, comparative electrochemical analysis enabled that the use of CNTs, template polymer and KOH activation have their own effect on this material’s superior electrochemical results including rate capability, cycle stability and high reversible capacity. This study not only analyze the synergetic roles between uniaxially packed CNTs and LTC, but also suggest the rational design of the ideal structure of CNT-based carbonaceous 1D anode material to maximize triple junction.

**ES07.08.04**

**Rational Design of 1D Partially Graphitized Nitrogen Doped Porous Carbon with Highly Aligned Carbon Nanotubes for Lithium-Ion Batteries**

Hanse In Cho, Yo Chan Jeong and Chong Rae Park; Seoul National University, Seoul, Korea (the Republic of).

The demand for high performance energy storage systems, such as electrical vehicles and electric storage stations has increased dramatically. Low temperature carbon (LTC) prepared at low temperatures (~1200 °C) and carbon nanotubes (CNTs) composite has attracted considerable attention due to LTC’s high reversible capacity and physical and chemical merits of CNTs, which supplement LTC’s structural instability and low electrical conductivity. Despite the recent advances in LTC-CNT electrodes, there are still remaining critical issues limiting commercialization. The most difficult one is controlling the state of CNTs in LTC since the aggregation of CNTs resulted in undesirable structure and increased electrical resistance. These aggregated CNTs also lower the surface coverage of CNTs within the LTC, interrupting the electrons on CNTs to meet ions in the LTC and consequently decreasing the accessible redox sites. Therefore it is essential to control the aggregation of CNTs in materials to fully utilize the merits of CNTs and guarantee the accessible redox sites, which is denoted as maximizing “triple junction” where ions and electrons meet, suggesting that the origin of the high electrochemical performance is the perfect harmony of ion, electron, and redox sites together.

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**ES07.08.05**

**New Hybrid Nano-Architecture of Li/Si Electrodes for Rechargeable Li-Ion Batteries**

Mariappan P. Paranthaman; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Novel Carbon Electrodes for Next Generation Intercalation Batteries

Carbon has recently been recovered from discarded tires and demonstrated a high capacity, higher rate capability and the potential to replace commercial graphite as an active anode material in lithium-ion batteries. The tailored morphology of the tire-derived carbon using a sulfonation process followed by pyrolysis yielded a high-quality carbon and the applicability of these hard carbons was demonstrated in several intercalation batteries including lithium-ion batteries, sodium-ion batteries, and potassium-ion batteries. We will report on our recent neutron studies on the surface chemistry of the carbon material, vibrational spectroscopy of the molecular structure, chemical bonding such as C–H bonding, and intermolecular interactions of the tire-derived carbon materials. Commercial graphite and unmodified/non-functionalized tire-derived carbon are also used for comparison. A capacity of over 200 mAh g\(^{-1}\) was achieved for carbon electrodes with Na-ion intercalation batteries. It is also possible to achieve even enhanced capacities by ball milling carbon with Si for Na-ion batteries. We will also report the current status of the tire-derived carbon composite powder scale up efforts and its use in energy storage applications.

**ES07.08.06**

**Novel Carbon Electrodes for Next Generation Intercalation Batteries**

Marjan Abadi; Imperial College London, UK; Jesus Martin; The University of Reading, UK; and Costel Cojocaru; 1Ecole Polytechnique, Palaiseau, France; 2CNRS, Palaiseau, France.

Today’s lithium-ion battery is the most maturing and widely used technology in the market. The optimization of the storage properties of batteries requires either the search for new materials offering specific capacities which are superior to current materials either the miniaturization of electrode materials. Incorporation of nanomaterials with high specific capacities has proven to be an effective method to improve the electrochemical performance of the lithium-ion battery. The present work explores a promising and original approach for the implementation and the development of a new bottom-up technique for hierarchical hybrid nanostructured electrodes based on vertically aligned carbon nanotubes (VACNTs) decorated with nanoparticles (NPs), i.e. NPs@VACNTs. The non-metallic lithium battery is composed of Li/Si@VACNTs as positive electrode and Si@VACNTs as negative electrode. This battery provides a theoretical energy of 1500 Wh kg\(^{-1}\), which is four times more than the theoretical energy of existing lithium-ion batteries based on LiCoO\(_2\) and graphite (~ 36 Wh kg\(^{-1}\)). Moreover, the nanostructured design of the two electrodes overcomes the problems associated with the use of sulfur compounds and silicon in lithium-ion batteries, including poor electrical conductivity and large volumetric variations. [1-2] This hierarchical hybrid nanostructured electrodes battery with low life and low cost shows a superior capacity of 2 mAh cm\(^{-2}\) based on the mass of the active material in the electrode.


**ES07.08.07**

**Metal Organic Framework Derived Metal Species Encapsulated into BCN Nanotubes for Energy Conversion and Storage Devices**

Hassina Tabassum and Zou Ruqiang; Peking University, Beijing, China.

Metal organic frameworks derived metal species have received great attention for boosting the performance of lithium-ion batteries because of their obvious advantages in solving the problems associated with large volume change, low conductivity, and short diffusion path for Li\(^{+}\) ion transport. A high concentration of B–N bonds in a carbon framework whereas the one with a lower molecular weight leads to B, N co-doped graphene nanotubes (BCN nanotubes) with segregated B–C and N–C bonds. Therefore, a universal strategy for making metal species like hollow transition metal oxide, metal phosphide, metal sulfide nanoparticles (NPs) encapsulated into BCN nanotubes through combining pyrolysis with extended treatment is adopted. The as-made products exhibit best performance for lithium-ion storage, electrocatalysts and supercapacitor devices. In this study, we tracked and studied the evolution of the structural defects with increasing accumulated metal species in the BCN nanotubes for electrocatalyst and lithium ion batteries. These results will help to efficiently optimized the best electrocatalysts and electrodes for lithium ion batteries.

References:


**ES07.08.08**

Dual Template-Assisted Fabrication of High-Surface-Area Hollow Carbon Nanospheres for Enhanced Energy Storage Mingei Chen, Zhe Su and Donghui Long; East
Hollow carbon spheres (HCSs) with diverse shell structures and inner space have attracted much attention owing to their wide applications in different fields such as adsorption, catalysis, energy storage, etc. Up to now, extensive synthetic strategies have been developed to obtain HCSs. Herein, we propose a dual-template assisted route, using volatile alkane as hollow-forming soft template and organosilane as in situ hard template for the first time. The obtained HCSs possess carefully controlled characteristics, including tailored outer diameters (0.5–1 μm), controlled shell thickness (50–100 nm), specific surface area (1500–2500 m² g⁻¹), and pore volume (1.5–2.7 cm³ g⁻¹). Adjustable pore structure of HCSs can realize function-oriented applications. When used as the electrode materials for supercapacitors, hierarchically porous HCSs demonstrate an energy density of 23 Wh kg⁻¹ at a high power density of 25 kW kg⁻¹. In addition, these HCSs can serve as sulfur host for Li-S battery, resulting in superior long-cycle stability and rate performance.

References
Moreover, the absorber can maintain its superior performance at 1000 K under air and 1173 K under vacuum, respectively. To the best of our knowledge, this performance achieved simultaneously when coated on various IR reflectors, including Au, stainless steel, Al, and TiN. Particularly, the absorbers with TiN reflectors exhibited a high solar spin-coating a perhydropolysilazane (PHPS) solution, acted as the protection and anti-reflection coating. Both full-spectrum sunlight absorption and strong IR reflection were absorption of sunlight around their resonance wavelengths. Due to the in-plane plasmonic coupling of close-packed TiN nanoparticles, the resonance wavelengths were able to red- and controllable sunlight absorption coating using well-dispersed colloidal TiN nanoparticles (20-80 nm). The absorption bandwidth, i.e., the cut-off wavelength, can be tuned been proven to exhibit stronger optical losses in the visible-near-infrared (NIR) range compared to traditional metallic plasmonic materials. In this work, we constructed a uniform Titanium nitride (TiN), as an emerging plasmonic ceramic material, offers tunable plasmonic properties, as well as excellent thermal and chemical stability. TiN nanoparticles have development of high-performance solution-processed selective absorbers is urgently demanded.

Concentrating solar power (CSP) plants and future solar thermochemical processes require high-performance solar absorber coating with suitable photothermal properties as well as high-temperature stability. Traditional coating materials are often lacking some of the desirable properties or are difficult to be tailored to meet various stringent requirements. While various nanostructures, including particles and multilayers, have been studied, they are often not stable at high temperature. Over the last few years, we have been developing spinel metal oxide nanostructures with tailored photothermal properties for solar absorber coating applications. These oxides have high melting points and are chemically stoichiometric, so they are expected to be stable in air at high temperature. First, we studied nanostructures of Cu(I) containing spinel oxide nanoparticles, including CuO-Cr$_2$O$_3$, Cu$_2$O-Cr$_2$O$_3$, Mn$_2$O$_4$, CuFeMnO$_6$, etc. These particles were made from either bottom-up hydrothermal or top-down ceramic processing. Coatings made of these Cu spinel oxide nanoparticles exhibit higher solar absorptance and more importantly, better high-temperature stability in air over an extended period of testing time (2000 hours), compared to the state-of-the-art coating Pyromark. The influence of chemical compositions, particle size, coating conditions on the optical properties will be discussed. Thermal stabilities are studied via photothermal property measurement and structural analysis. Second, we explored new morphologies of metal oxide nanostructures, including nano-needles and nano-flowers. These unique structures can possess record-high solar absorptance (over 99%) even with very thin coating, owing to the strong light trapping effect. With suitable chemical compositions and surface passivation, the nanostructures can maintain their structural integrity at high temperature in air. The structures can be further tailored to show vastly different infrared properties. Finally, we showed that the recent high-entropy alloy concept can be applied to the spinel metal oxides to synthesize entropy-stabilized oxides, which may provide a new route to achieve unprecedented high-temperature stability for future solar-thermal coatings. Our studies demonstrate that nanostructures of spinel metal oxides offer tremendous opportunities for future high-temperature solar-thermal coating applications, by providing both high performance and excellent high-temperature stability.

Next-generation concentrating solar power (CSP) plants and future solar thermochemical processes require high-performance solar absorber coating with suitable photothermal properties as well as high-temperature stability. Traditional coating materials are often lacking some of the desirable properties or are difficult to be tailored to meet various stringent requirements. While various nanostructures, including particles and multilayers, have been studied, they are often not stable at high temperature. Over the last few years, we have been developing spinel metal oxide nanostructures with tailored photothermal properties for solar absorber coating applications. These oxides have high melting points and are chemically stoichiometric, so they are expected to be stable in air at high temperature. First, we studied nanostructures of Cu(I) containing spinel oxide nanoparticles, including CuO-Cr$_2$O$_3$, Cu$_2$O-Cr$_2$O$_3$, Mn$_2$O$_4$, CuFeMnO$_6$, etc. These particles were made from either bottom-up hydrothermal or top-down ceramic processing. Coatings made of these Cu spinel oxide nanoparticles exhibit higher solar absorptance and more importantly, better high-temperature stability in air over an extended period of testing time (2000 hours), compared to the state-of-the-art coating Pyromark. The influence of chemical compositions, particle size, coating conditions on the optical properties will be discussed. Thermal stabilities are studied via photothermal property measurement and structural analysis. Second, we explored new morphologies of metal oxide nanostructures, including nano-needles and nano-flowers. These unique structures can possess record-high solar absorptance (over 99%) even with very thin coating, owing to the strong light trapping effect. With suitable chemical compositions and surface passivation, the nanostructures can maintain their structural integrity at high temperature in air. The structures can be further tailored to show vastly different infrared properties. Finally, we showed that the recent high-entropy alloy concept can be applied to the spinel metal oxides to synthesize entropy-stabilized oxides, which may provide a new route to achieve unprecedented high-temperature stability for future solar-thermal coatings. Our studies demonstrate that nanostructures of spinel metal oxides offer tremendous opportunities for future high-temperature solar-thermal coating applications, by providing both high performance and excellent high-temperature stability.

Developing solar absorber coatings that can absorb sunlight while enduring high temperatures is a challenging task, but they can be successfully synthesized with careful engineering. Our team has recently designed an ultra-absorptive array of cobalt oxide nanoneedles. This cobalt oxide nanoneedle array is spectrally selective and its nanostructure increases the optical pathway of light, allowing the coating to possess over 99% solar absorptance; however, it is fragile, and degrades at high temperatures. Through altering the chemical composition and adding passivating layers, the nanoneedle maintains its distinctive shape, even after long-term high-temperature annealing. In this talk, we will also analyze the solar-to-thermal energy conversion efficiency before and after long-term thermal annealing.

Concentrating solar power (CSP), as a well-known high-temperature solar-thermal technology, is a promising approach to harvesting solar energy due to its efficient utilization of full-spectrum sunlight, and high availability in energy storage. To further pursue higher Carnot efficiency and greater cost reduction, next-generation CSP plants operating at higher temperatures (≥1000°C) are widely accepted as a promising approach. A selective solar absorber, as a critical component in CSP systems, is required to maintain high sun light absorption and low absorption (i.e., emission) beyond a cut-off wavelength in the infrared region to avoid thermal re-radiation even at elevated temperatures. To date, all the state-of-the-art selective absorbers such as cermet and photonic crystals with superior performance (i.e., high selectivity and great thermal stability) were manufactured with complicated and expensive high-vacuum micro-fabrication or nano-fabrication techniques, leading to high costs and challenges for largescale deployment. Therefore, the development of high-performance solution-processed selective absorbers is urgently demanded.

Titanium nitride (TiN), as an emerging plasmonic ceramic material, offers tunable plasmonic properties, as well as excellent thermal and chemical stability. TiN nanoparticles have been proven to exhibit stronger optical losses in the visible-near-infrared (NIR) range compared to traditional metallic plasmonic materials. In this work, we constructed a uniform and controllable sunlight absorption coating using well-dispersed colloidal TiN nanoparticles (20-80 nm). The absorption bandwidth, i.e., the cut-off wavelength, can be tuned through rationally controlling the concentration of the TiN colloid and the spinning speed. The excited plasmonic resonance of TiN nanoparticles resulted in highly selective absorption of sunlight around their resonance wavelengths. Due to the in-plane plasmonic coupling of close-packed TiN nanoparticles, the resonance wavelengths were able to red-shift to NIR range. As a result, selective sunlight absorption can be attained in the UV-visible-NIR range below the cut-off wavelength. An amorphous SiO$_2$ layer, prepared by spin-coating a perhydropolysilazane (PHPS) solution, acted as the protection and anti-reflection coating. Both full-spectrum sunlight absorption and strong IR reflection were achieved simultaneously when coated on various IR reflectors, including Au, stainless steel, Al, and TiN. Particularly, the absorbers with TiN reflectors exhibited a high solar absorptance of 93.5% and a low IR emittance of 21.1% at an elevated temperature of 1000 K, producing a solar-thermal energy conversion efficiency of 81.3% under 100 suns. Moreover, the absorber can maintain its superior performance at 1000 K under air and 1173 K under vacuum, respectively. To the best of our knowledge, this performance
surpasses or equals those of state-of-the-art selective absorbers fabricated by high-vacuum micro and nano-fabrication techniques. The high efficiency and great thermal stability achieved in such low-cost solution-processed solar absorbers will benefit the development of next-generation CSP plants by providing large cost reductions in mass-production.

4:30 PM *ES08.02.04
Black Oxides in the Spinel Group—Promising Materials for Highly Durable Solar Selective CSP Absorber Coatings Andreas Schuler; Solar Energy and Building Physics Laboratory, Swiss Federal Institute of Technology EPFL, Lausanne, Switzerland.

In this presentation I will review some recent developments in the field of black spinel-type oxides for solar selective absorber coatings. The interesting optical properties of ternary and quaternary spinel-type oxides allow for manifold interband transitions, yielding a dark or even black appearance of many spinel oxides, which show remarkable stability at elevated temperature in air and vacuum. In order to overcome the barrier of initial investment cost, wet-chemical derived solar absorber coatings might be especially attractive. By sol-gel dip-coating and subsequent thermal annealing, we produced multilayered mixed Cu-Co-Mn-Si oxide [1,2]. After optimization of the multilayer design, a solar absorbance of 0.95 and a thermal emissivity of 0.12 at 100 °C have been achieved. For the energy-efficient thermal annealing of 2 m long receiver tubes, a special induction heating process has been developed. On highly infrared-reflecting substrates, spinel oxide based layer stacks can be very selective. For a three layer configuration composed of a CuMnO thin film and two consecutive antireflective coatings, FeMnCuO4 and SiO2 on aluminum substrates, a solar absorbance of 0.957 and a thermal emissance of 0.290 were measured at 100 °C achieved [3]. Aiming at operation temperatures of up to 550 °C, the absorptance of the multilayer structure coated through this way increased from 0.82 to 0.915 and the thermal emissance decreased from 0.434 to 0.290. Defects on the surface of WC-Co coatings were gradually reduced, the multilayered film stacks were compact and the surface roughness was reduced [4]. Copper-oxide spinel coatings can alternatively be deposited by spray-coating. Black metal oxide nanoparticles comprising copper-cobalt oxides (CuCoO4) and copper-manganese oxides (CuMnO4) were synthesized for solar absorptive potential by hydrothermal syntheses. To extend the spectrally-selective absorbance capability, the coating surfaces are geometrically-textured, using sacrificial polymer beads that are jointly implemented in the spray-coating process [5]. Also crystalline CuNiCo3Ox films have interesting optical properties. By optimizing the concentration of the solution, withdrawal speed and annealing temperature, a solar absorptance of 0.91 and an emittance of 0.14 were achieved for a single layer coating with composite oxide formation [6]. The remarkable stability at elevated temperatures in air and vacuum makes such black spinel oxide coatings an interesting candidate for solar applications involving concentrated solar radiation, such as the generation of solar electricity (concentrated solar power CSP), industrial process heating and solar cooling.

SESSION ES08.03: Corrosion Mitigation in CSP Plants
Session Chairs: Elena Guillen and Andreas Schuler
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 123

8:45 AM ES08.03.01

Over the past seven years, the US Department of Energy has developed a framework where chloride based salt eutectics can serve as the heat transfer fluid and thermal energy storage medium in concentrating solar power (CSP) plants at a cost competitive with traditional power plants in the United States. However, catastrophic corrosion remains the highest risk to this framework. A series of completed and ongoing research and development initiatives have significantly evolved the understanding of corrosion control in chloride salt systems. These have brought to focus viable corrosion mitigation strategies and system requirements for an operable power plant at the megawatt scale. This work presents these integrated results and describes a path from present day understanding into the next generation of CSP plants.

9:00 AM *ES08.03.02

The United States Department of Energy (DOE) launched the SunShot Initiative in 2011 to achieve high thermal-to-electric conversion efficiency and to make solar technologies cost-competitive with conventional electric power generation. The sun’s energy is captured and stored in the form of heat in concentrating solar power (CSP) technologies. By using low cost materials that are stable for decades, CSP with the help of thermal energy storage (TES) systems is able to deliver renewable energy while providing important capacity, reliability and stability attributes to the grid, thereby enabling increased penetration of variable renewable electricity technologies. Current CSP systems are integrated with conventional steam-Rankine power cycles. Today’s advanced technologies are power tower with 2-tank molten-salt TES, delivering thermal energy at up to 655°C using molten nitrates. Next generation CSP (Gen3 CSP) are targeting higher efficiencies by integrating the power tower with the TES to a supercritical CO2 (scCO2) Brayton power cycle. To achieve this integration, Gen3 CSP needs to operate at temperatures above 550°C requiring high-temperature advanced fluids in the range of 550°C to 750°C. Because nitrates are unstable at temperatures above 60°C, new salts are required. These high-temperature salts, such as chlorides, need to compatible with containment materials. To meet the cost of production of electricity, cost targets must be met using alloys and materials with acceptable corrosion and mechanical strength. The selected heat transfer fluid (HTF) candidates based on cost are chlorides, but they introduce a set of technological and engineering challenges because of their very corrosive characteristics for typical materials. Corrosion mitigation approaches are been investigated to control material’s degradation below 20 μm/year. Corrosion in molten chlorides is being controlled in atmospheres with the absence of oxygen and water. Catastrophic mechanical failure will occur if these impurities are present because intergranular attack will occur. Current studies are focused on: 1) redox potential control using active metals in atmospheres with no-oxygen/water; 2) surface treatments to allow passivation, diffusion coatings; 3) coatings such as nickel-based (NiCoCrAlY,Ta,Ha,Si); and 4) aluma forming alloys (AFA). Untreated In800H and 3108S alloys corrode rapidly (~2,500 to 4,500 μm/year) in molten chlorides, but when coated the lowest corrosion rate of 190 μm/year is obtained. Because the coatings were pre-oxidized before molten salt immersion, metallographic characterization of showed that the formation of a uniform thin alumina scale. The presence of this layer presumably reduced the corrosion of the alloy in the molten chloride in an atmosphere containing oxygen and water as impurities. Electrochemical impedance spectroscopy tests and metallographic characterization showed that the best performing AFA in molten chlorides without controlled atmosphere was Inconel 702 pre-oxidized in zero air (ZA) at 1045 °C, due to the formation of protective, dense and continuous alumina layers. When using an argon atmosphere during corrosion evaluations, these layers were unstable. AFAs to contain molten chlorides in air are promising for Gen3 CSP applications because protective alumina layers were stable and able to grow from 5 μm (before immersion) to 13 μm (after 185 h of immersion) in the oxygen-containing atmosphere. The use of these alloys could be commercially feasible and cost-effective because of the possibility of using oxygen-contaminating atmospheres instead of keeping enclosed systems with inert atmospheres to protect alloys from corrosion in molten chlorides.

9:30 AM ES08.03.03
Nickel-Aluminide Based Anticorrosion Coatings Prepared by Plasma Spray for Concentrating Solar Power Applications Sarah Yasin; Jose I. Endrino1, Elena Guillen2, Ramon Escobar Galindo3 and Adrianus I. Aria1; Cranfield University, Cranfield, United Kingdom; 2Profactor GmbH, Steyr, Austria; 3Universidad de Cadiz, Cadiz, Spain.

The use of solar energy for power generation provides an efficient sustainable energy solution. Among a number of technologies developed for power generation using solar energy, concentrating solar power (CSP) is encouraging because of the capability of thermal energy storage that makes it possible for the 24-hour energy production. Although the use of molten salts as heat transfer fluid and thermal storage in CSP has various advantages, they have a major disadvantage as they make the component systems highly susceptible to corrosion. Different approaches have been adopted to suppress hot corrosion including the use of high alloy steels and the use of high purity molten salts; both contribute to a substantial increase in construction and operating costs.

In this study, we investigate the use of protective coatings to enhance the corrosion resistance of the component systems against molten salts at an elevated temperature. Nickel aluminide coatings are deposited using highly scalable plasma spray technique with few different deposition parameters to obtain a variety of stoichiometries and morphologies. A low value of porosity is anticipated for corrosion resistance along with good adhesion with substrate, minimum unmelted-particles and adequate lamellar structure for optimum coatings. Optimized coatings deposited on SS347 and SS304 stainless steel substrates were exposed to a mixture of NaNO3 / KNO3 molten salts at 600°C for up to 2500 hours. The uncoated
substrates were also included in the test for comparison. After the test, the samples were characterised by electron microscopy, energy dispersive x-ray spectroscopy, and x-ray diffraction to evaluate their corrosion behaviour. In this presentation, the corrosion test results and the potential of nickel aluminate coatings to suppress hot corrosion by molten salts in an environment that simulates that of concentrating solar power plants will be presented and discussed.

9:45 AM ES08.03.04  
Nanostructured Solid Ionic Hydrogen Barrier Coatings—Engineering Defect Chemistry and Interfaces for Corrosion Resistance  
William J. Bowman, Jing Yang, Xiaohui Yao and Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Hydrogen embrittlement of metallic components is a leading cause for corrosion failure in high-temperature heat-exchange systems, whose components operate in extreme environments. Hydrogen is a byproduct of corrosion in water- or H2S-containing environments commonly associated with heat transfer media employed in high-temperature heat-exchange systems. To mitigate surface corrosion, protons should ideally be discharged from the solid-liquid interface into the liquid phase as gaseous H2. Though some atomic and/or ionic H is absorbed by the solid as point defects, ultimately inducing embrittlement and making the metal increasingly susceptible to fracture. For H uptake to occur, it must penetrate a synthetic or native surface layer (e.g. oxide, sulfide, carbonate), which involves interfacial and bulk solid-state ionic processes, including surface adsorption and absorption, as well as bulk diffusion. Hence, there is a significant opportunity to elucidate these processes, and to engineer solid ionic barrier coatings that mitigate H uptake and embrittlement in high-temperature thermal energy systems and metal components employed elsewhere.

Here we aim to develop a solid ionic H barrier coating by employing design and engineering approaches to (i) minimize the H point defect solubility and mobility in the coating material, and (ii) elucidate the role of interfaces in corrosion barriers during the H blocking process. We employ a doping strategy for a model non-stoichiometric oxide monoclinic ZrO2 following a recently-developed theoretical framework based on density functional theory and statistical thermodynamics that predicts point defect concentrations in metal oxides, including H point defects [1]. We measured electrical conductivity and H solubility in doped monoclinic ZrO2 compositions that had not be reported prior, and these experiments provided quantitative and qualitative validation of the theoretical modeling framework [2]. Temperature programmed water desorption was employed to quantify H solubility in these oxides and to elucidate the nature of H defects. Doping was found to effectively modulate hydrogen solubility in ZrO2, and we modified the oxide microstructure and performed solubility measurements under varied oxygen partial pressure to elucidate the H-containing defects, and to illustrate the influence of porosity and grain boundaries on H pick-up. Additionally, we electrochemically investigated the H flux through oxide thin film coatings grown on steel, with the intention of investigating the impact of solid-liquid interfaces and microstructure on H barrier coating performance.

Acknowledgements  
We gratefully acknowledge the MIT Energy Initiative and Equinor Inc. for financial support.

References  

10:00 AM BREAK

SESSION ES08.04: Solar Optical Components  
Session Chairs: Javier Barriga and Matthias Krause  
Thursday Morning, April 25, 2019  
PCC North, 100 Level, Room 123

10:30 AM †ES08.04.01  
Aging Models of Environmental Stress Factors for Solar Mirrors Lifetime Prediction  
Olivier Raccurt1, Coralie Avenel1,2, Sandrine Therias2 and Jean Luc Gardette2; 1Univ Grenoble Alpes, CEA LITEN, Grenoble, France; 2Univ Clermont Auvergne – CNRS – SIGMA Clermont, ICCF, Clermont-Ferrand, France.

The durability of solar mirrors is a critical factor for the deployment of concentrating solar power (CSP) plants [1,2]. Accelerated aging models currently applied in the polymer, electronic and photovoltaic fields have recently been reviewed [3], and the issues of their application to solar mirrors have been discussed. Lifetime prediction of solar mirror requires determining the kinetic laws of the degradation related to the stress factors level and the associate models. Temperature and humidity has been identified to be major stress factors for solar mirrors [4-6]. Accelerated aging in temperature and temperature with humidity at different levels were performed to assess the dependent parameters of models selected from the literature. Results from three different mirrors technology will be presented and analyzed to extract kinetics parameters for models. These parameters include the apparent activation energy for the Arrhenius temperature law, the Peck and Eyring coefficients for humidity. The experimental values were then assessed for specular reflectance loss of solar mirrors. Finally, using these parameters, acceleration factors were calculated for solar mirrors. An effective temperature taking into account the Arrhenius degradation law was used rather than the commonly used mean temperature. The relevance and utility of this effective temperature compared to a simple mean have already been discussed in the literature [7-9]. The problem of coupling all previous laws together is also addressed. Finally, a calculation of acceleration factor related to different CSP sites around for standard dump heat test (85°C, 85%RH) will be presented and discussed.

References  

11:00 AM ES08.04.02  
WITHDRAWN 4/4/2018 ES08.04.02 Hydrophobic CaF2 Film for Anti-Reflective Applications  
Raxish K. Jain1, Iatinder Kaur1, Atul Khamma1 and Amit K. Chawla2; 1Physics, Guru Nanak Dev University, Amritsar, India; 2Center of Nanoscience & Nanotechnology, University of Petroleum & Energy Studies, Dehradun, India.

Thin films of CaF2 were deposited on microscopy glass substrates by thermal evaporation and their structural, optical, and wettability properties were characterized. Thin films of the well-known anti-reflective material MgF2 were also synthesized and their optical and wettability properties were compared to those of CaF2. X-ray diffraction studies showed that CaF2 films are crystalline whereas MgF2 films are amorphous. The cross-sectional FESEM images found that the thickness of the CaF2 and MgF2 films were in the range of 100-130 nm. The optical transmittance and reflectance properties were studied by UV-vis spectrosopy. The average specular reflectance values were 10.8%, 7.9% and 8.6% for bare glass slide, MgF2 and CaF2 coated samples respectively, which showed that both films have good anti-reflecting properties. The water contact angle measurements were carried out to study the wettability properties of the samples and both CaF2 and MgF2 films were found to be hydrophobic with an average water contact angles of 131±2° and 98±2°, respectively. It is concluded that CaF2 films have a very good potential to be used as hydrophobic anti-reflecting coatings. The water contact angle of CaF2 film sample is...
significantly higher than that of MgF₂ film which makes the former more suitable for applications in eye lenses, car wind-shields and coatings on covering glass of solar cell panels and display devices where hydridic coating with low optical refraction is required.

11:15 AM *ES08.04.03 Monolithic Glass-Based Antireflective Coatings—Broadband/Omnidirectional Light Harvesting and Superhydrophobic Anti-Soiling Characteristics

Tokyo Aoyagi, Andrew Lupini, Poornan Joshi, Ilia N. Ivanov, Rajesh Menon; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; The University of Utah, Salt Lake City, Utah, United States.

Mitigation of the soil accumulation is imperative to decrease the maintenance cost while increasing the long-term energy efficiency and energy generation of solar power installations. Here we describe the formation of atomically bonded, optical-quality, nanostructured porous thin glass film coatings, utilizing metastable spinodal phase separation in a low-alkali borosilicate glass system. The coatings, which are optically imperceptible, simultaneously provides graded-refractive-index antireflectivity and superhydrophobic anti-soiling capabilities, with excellent mechanical durability. In particular, through its inherent antireflective characteristics, these nanostructured surfaces are found to promote a general and an invaluable 3–7% relative increase in current output of multiple direct/indirect bandgap photovoltaic cells. Besides, the coatings maintain optical transparency and superhydrophobic attributes when subjected to simulated sand/dust-storm conditions (based on NOAA reported conditions in desert environments). The present concept represents a fundamental basis for development of advanced coated optical quality products that can significantly improve the performance of CSP components.

11:30 AM *ES08.04.04 Design and Optimization of Solar Thermo Electric Energy Conversion Devices

Siddarth Viswanathan, Tristan Emm, Peter Thomas and Rama Venkatasubramanian; Novus Energy Technologies, Cary, North Carolina, United States.

Solar thermal energy to electric power conversion can be a very cost effective and scalable approach to harnessing the abundant solar energy. Solid state thermo-electric devices are reliable, scalable, and can be made cost-effectively for low $/Watt scenarios. In contrast to solar PV systems, solar-thermoelectric devices can offer high electric power density (W/unit area of active semiconductor), can be made to operate even when sunlight is not available using thermal storage systems, and particularly, in addition to providing electric power, can also provide hot-water from the heat that is not converted to electric power. As a low-cost route to solar thermo-electric conversion demonstration, we will report on our early studies in developing a solar thermo electric generator (STEG) system. We used a 1 m² Fresnel lens to collect direct solar light over a large area and directed it onto a ~0.01 m² area thermo-electric generator modules (TEG), equivalent to a x100 concentration. The planar Fresnel lens was not coated with any anti-reflection coating in these early studies, but are planned. The TEG modules consisted of ~300 °C-capable Bi₂Te₃-based modules, arranged in a linear 1.5 m x 4 m array. Since all the heat impinging on the TEGs is not converted to electric power, we developed a water-based heat removal system on the cold-side of the TEG modules. The thermal management system consisted of a circulating water loop and a heat-rejection finned heat-sink with a fan. The testing of the STEG module was conducted outdoors. Without any high-emissive (i.e., absorptive) coating on the TEG hot-side, the STEGs produced a voltage of 2.14 V. Even with a modest improvement in emissive/absorptive coating, for the same Fresnel lens configuration, we noted a significant increase in the voltage output to 5.72 V. The x2.7 increase voltage output, with essentially the same internal electrical resistance of the TEG module, would translate into x7.2 more power output. Under extremely sunny conditions, we have observed that the voltage output could go up to 8 V. Clearly, the influence of the heat-absorption coatings on the TEG modules indicates the need for further optimization as well as anti-reflective coating on the front-end planar Fresnel lens light focuser. With further optimization of Fresnel lens geometries, absorptive coatings, and thermal resistance of the TEG devices, higher temperatures can be obtained on the hot-side and therefore higher Carnot efficiencies can be obtained. For these applications, Novus is developing scalable, large-area high-temperature TEG modules based on half Heusler materials. We believe the STEG approach is an attractive way to harness the abundant solar energy in a scalable and cost-effective way.

11:45 AM *ES08.04.05 Low-Cost, High-Efficiency Concentrated Solar Heat System Based on Nano- and Microstructured Polymer Lenses Fabricated by Roll-to-Roll Extrusion Coating

Maria Matschuk and Henrik Pranck; Heliax ApS, Horsholm, Denmark.

Heliax has developed a concentrator concept largely based on modified, but well-known industrial processes. The solar concentrator itself consists of a Fresnel-like lens made in a thin polymer film which is glued onto planar glass for geometrical stability. The lens with focal distance of 2 meters focuses the light onto a heat-exchanger type flat receiver made by the welding of two corrugated steel plates, forming channels where a circulating liquid will be heated by the incident sunlight. Both components are fixed on a dual axis solar tracker, each holding 8 lenses and receivers. Advantages of the system are many; a flat lens greatly reduces the wind cross section (when positioned in horizontal mode), reducing the strength requirements for the whole structure, including the foundation. Flat lenses also make cleaning easier, and simplifies logistics compared to e.g. parabolic mirrors.

Furthermore, the two-dimensional focusing reduces the precision requirements from tens of millidegrees to degrees, allowing for use of low-cost gear-motors. Also, the acceptance angle of the sunlight is much higher than on mirror-based systems, as the result of combined two-dimensional focusing and a refractive lens. We have measured an acceptance angle of approximately 7 degrees, which is a large advantage if there is atmospheric spreading of the light, either due to cloud cover or smoggy conditions. All these advantages sum up to a much lower cost, where expected sales price is in the range of 350€/kWp(thermal) to 450€/kWp(thermal) depending on plant size. Installation is fast, and the system is modular. First plant for district heating (95°C) are being brought in operation Q1 2019. Next plant will feature a higher operating temperature (350°C) and for that partners and solutions to implement higher temperature operation are sought.

SESSION ES08.05: High Temperature Solar Receiver Coatings
Session Chairs: Renkun Chen and Sungho Jin
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 123

1:30 PM *ES08.05.01 Spectrally Selective Coatings for Thermosolar Power Plants Working at High Temperatures

Javier Barriaga, IK4-TEKNIKER, Eibar, Spain.

The optimisation of solar selective coatings (SSC) for solar receivers plays a critical role in the efficiency of a concentrated solar power (CSP) plants. In this work two different SSC has been developed: one of them to operate in vacuum for parabolic through collectors (PTC) and the other to operate in air for linear Fresnel collectors. The final achieved multilayer stack designs were obtained after a combination of PVD parameters optimisation, characterisation and optical simulation of the individual layers. Multi-layered coating for evacuated receivers: SiO₂/AIW/Mo/W deposited using magnetron sputtering showed excellent optical selective properties α = 94.0% and εdash = 4.8% and long-time thermal stability at the operation temperature of CSP plants. SSC has been scaled up to 4 m long tubes and its efficiency is going to be tested in real plant. Chromium oxynitrides, AlCrO/AICrON/AlCrN deposited by magnetron sputtering were selected to develop solar selective coating to operate in air due to its exceptional thermal stability and oxidation resistance at high temperatures. Again, excellent optical selective properties, total solar absorptance above 90% and thermal emittance below 10% were measured. Thermal stability of the coatings was tested by means of an accelerated ageing test based on Arrhenius calculations.

2:00 PM *ES08.05.02 Multilayer Multifunctional Advanced Coatings for Receivers of Concentrated Solar Power Plants

Ludovic Charpentier, Danying Chen, Johann Colas, Frédéric Mercier, Michel Pons, Didier Pique, Gaël Giusti and Marianne Balat-Pichelin; PROMES, CNRS, Font-Romeu Odeillo, France; SIMAP, Université Grenoble-Alpes, CNRS, Grenoble INP, Grenoble, France; Siltronix ST, Archamps, France.

The extending market of the concentrated solar power plants requires the use of high-temperature materials for solar surface receivers that would ideally heat an air coolant beyond 1300 K. The currently used Ni-based alloys present operating working points between 970 and 1070 K as severe damages due to oxidation would occur beyond these temperatures and therefore a complementary heating of the coolant using fossil source or biomass is required. Ceramics like SiC are resistant to oxidation at higher temperatures (1470 to 1770 K), but are sensible to cracking that would quickly break the solar module. The collaborative project “Multilayer Multifunctional Advanced Coatings for Concentrated Solar
Ultrathin Silicon Carbide-Metal Nanocomposites as High Temperature Solar Selective Coatings

In this paper, we discuss the high temperature (up to 800 °C) performance of metallic absorbers. We present the results of short high temperature oxidation (up to 80 minutes) performed in solar furnaces and compare them to the ones of longer oxidation tests (up to 1,500 h) performed in industrial furnaces. These results will be shown and discussed. In addition, the coatings were tested under solar facilities available at PROMES-CNRS in Odeillo, France, to perform high temperature cyclic oxidation in air with thermal shocks (temperature rates during heating and cooling are up to 100 K s⁻¹) using the “Reacteur Hautes Pression et Température Solaire” (REHTPS), and high temperature optical measurements using the “Moyen d’Essai et de Diagnostic en Ambiance Spatiale Extrême” (MEDIASE). Room temperature optical measurements were also performed to investigate the consequences of the high-temperature treatments on the optical properties of the materials. Structural characterizations were performed using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM/EDS), X-Ray Diffraction (XRD) and micro-Raman analyses in order to identify surface evolution and damages due to high temperature oxidation. The results of short high temperature oxidation (up to 80 minutes) performed in solar furnaces were compared to the ones of longer oxidation tests (up to 1,500 h) performed in resistive furnaces.

The first results showed the difficulties to protect TZSM from fast oxidation: smokes of gaseous molybdenum oxide appeared from 670 K due to grain boundary diffusion through the coating. Tests on aluminate and silicide coatings are going on in order to add an additional barrier to Mo and O₂ diffusion. Kanthal APMT™ supports oxidizing atmospheres at 1400 K due to the formation of a protective layer mainly made of alumina. AlN and SiC/AlN coatings slightly changed the oxidation resistance and improved the solar absorbance of the substrate. After oxidation and the built-up of an oxide layer, this improvement was maintained. Nevertheless, the coatings cracked after a few fast thermal shocks from 1400 K to 900 K. According to our simulations, this is the result of high stress levels (2.5 GPa) that go beyond the failure limit of the coating (1.8 GPa). High temperature oxidation resistance and optical properties of metallic alloys were improved by the different coatings. However, the high temperatures reached (> 1300 K) led to a rapid diffusion of oxygen and alloying elements of the refractory alloy and the fast thermal shocks led to high stress levels not compatible with metal-ceramic systems with large differences in thermal expansion coefficients.

2:15 PM ES08.05.03
Microstructural and High-Temperature In-Air Stability Study of Solar Absorber Coatings Based on Aluminum Titanium Octynitrides Irene Heras, Matthias Krause, Gonzalo Rincon, Elena Guillen Ibañez, Ibon Azkoná, Frank Luzgitz, Daniel Janke, Franz Munnik, Jose Carlos Rodriguez, Jesus Fernandez and Ramon Escobar Galindo

The development of Generation 3 (GEN3) C-based solar absorber coatings implies an increase of the temperature of the heat they deliver to the power cycle in order to increase the plant efficiency and lower the costs. In particular, current central tower systems operate at maximum temperatures of 550 °C mainly due to the severe degradation that the state of the art absorber paints (i.e. Pyromark®) suffer at higher temperatures. In previous works [1,2] aluminum titanium oxynitrides Al₆Ti₄N(O,N)₂ were shown to be excellent candidate materials for solar selective coatings (SSC). These results confirmed that the designed SSCs based on these materials withstand breakdown at 600 °C in air after 900 hours of thermal cycling. In this paper, we discuss the high temperature (up to 800 °C) stability of a solar absorber based on Al₆Ti₄N(O,N)₂ deposited by cathodic vacuum arc (CVA) at higher working pressure (P = 2.1 Pa) than those discussed in [1] and [2]. The composition, morphology and microstructure of the films were characterized by ion beam analysis, scanning and transmission electron microscopy and X-ray diffraction. The optical properties were determined by ellipsometry and spectrophotometry (UV-Vis-NIR, FTIR). The microstructural and spectroscopic characterization shows the formation of a solid solution of Al₂O₃/TiN crystalline nanoparticles embedded in an amorphous Al₂O₃(N,N)₂ matrix. This microstructure provides the coating with a high absorption coefficient within the whole wavelength range of interest (0.3 to 25 μm) as modeled by spectrophotometric ellipsometry. Hence, this single layer absorber shows an absorption, α, of 92% and an emissivity, ε_RT, of 70%. The addition of an antireflective Al₂O₃ layer and post-deposition treatments improved the optical properties of the absorber to better values (α = 96% and ε_RT = 60%) than those of Pyromark®. The thermal stability in air of the absorber was firstly analyzed by cyclic heating tests, showing no degradation after 300 h of cycles in air at 700 °C. Subsequently, the samples were tested in a solar furnace at 650 °C and 800 °C for 12 hours at environmental conditions. Therefore, this oxynitride nanocomposite absorber coating presents the best thermal in-air stability studied so far by our group.


2:30 PM ES08.05.04
Ultrathin Silicon Carbide-Metal Nanocomposites as High Temperature Solar Selective Coatings Aikifia Raza, Ruhong Gao, Afira S. Alketbi and TieJun Zhang; Department of Mechanical and Materials Engineering, Masdar Institute, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates.

Solar thermal technologies, converting the abundant solar energy into heat and electricity, have attracted extensive attention in recent years. It is desirable to increase the operating temperature of concentrated solar power plants for higher conversion efficiency, which requires the design of high-temperature components and, in particular, the solar absorber coatings. Recent advances in photochemical conversion, the solar absorber surface must have high solar absorptance (α ≥ 0.98) and a low thermal emittance (ε ≤ 0.05) at the operational temperature (T ≥ 500 °C). For this purpose, we propose spectrally selective SiC-metal (Si-M) based nanocomposite absorbers with low infrared emissivity above 500 °C. The as-fabricated ultrathin nanocomposite absorber with sandwich-like configuration, consisting of SiC/SiC-M/SiC on reflective layer coated on stainless steel substrate, has exhibited an absorptance of 80-85% in the wavelength range of 280-2000 nm. The surface plasmon polaritons of metal inclusion within the SiC matrix of ultrathin nanocomposite layer have contributed to the broadband light absorption, while the top most layer of SiC acts as anti-reflection layer. The bottom reflective layer of tungsten coated on stainless steel substrate reduces the infrared emittance and improves the thermal stability of the absorber. With the exceptional thermal shock resistant and anti-corrosive properties of SiC as well as the rational design of metal inclusions in the SiC matrix, the proposed absorber can achieve near-perfect absorption in the solar spectrum and also get truncated with a sharp slope in the infrared region for mid to high temperature solar thermal applications.

2:45 PM ES08.05.05
High Temperature In-Air Stability Studies of SnO₂:Ta Thin Films Used as Solar-Selective Transmitter in CSP Ahvarto Méndez Fernández, Iván Fernández Martínez, AmbÚrn Wenneberg, Sandra Muñoz Piña, Jose Carlos Rodriguez, Frank Luzgitz, Daniel Janke, Ramon Escobar Galindo and Matthias Krause; 1NANOENERGY SLNE, Madrid, Spain; ²NanoComposite Division - Ion Beam Center, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany; 3Concentrating Solar Systems Unit, CIEMAT - Plataforma Solar de Almería, Tabernas, Spain; 4Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, IEEMYAT - Universidad de Cádiz, Puerto Real, Spain.

The importance of finding more effective and cleaner ways of producing energy other than fossil fuels is growing fast in order to reduce CO₂ emissions that contribute to the greenhouse effect. Concentrating solar power (CSP) uses reflectors to redirect and concentrate the solar radiation onto a receiver, where it is transformed into heat. Downstream heat exchangers and gas turbines are the final elements of the plant responsible for transforming the heat into electricity. Current CSP plants are operated at a maximum of 550 °C, but an increase of the operation temperature to 800 °C, in combination with solar-selective coatings, would significantly improve their efficiency by more than 10 %. In order to approach this issue, a transparent conductive oxide (TCO) thin film based on SnO₂ doped with Ta was developed and optimized by reactive magnetron sputtering [1]. This material was shown resisting 800 °C in vacuum for 4 hours, transmitting incident sunlight and blocking infrared emission from the underlying blackbody absorber. As such, it exhibits all properties required of a solar-selective transmitter for high-temperature CSP usage. In this work, thermal stability tests were carried out in air using an electric furnace for a total of 12 hours at 650 °C and 800 °C, respectively, for laboratory samples and industrially produced coatings. These results will be shown and discussed. In addition, the coatings were tested under environmental conditions at 650 °C and 800 °C in a solar furnace, again for a total of 12 hours each, providing information about their behaviour and performance in a situation much closer to the final application. Spectrophotometry, Rutherford backscattering spectrometry and conductivity measurements, among other techniques, were used to track the evolutions of the properties and performance of SnO₂:Ta thin films under these conditions.


This work was supported by the EU H2020 RISE project “Framework of Innovation for Engineering of New Durable Solar Surfaces” (FRIENDS®, GA-645725).
Preparation and Characterization of Solar Thermal Absorbers by Nanoimprint Lithography and Sputtering

Tina Mitteramskogler\textsuperscript{1}, Amböörn Wennberg\textsuperscript{2}, Iván Fernández Martínez\textsuperscript{2}, Felipe Tessarollo Ramos\textsuperscript{1}, Michael J. Haslinger\textsuperscript{1}, Michael M. Muehlberger\textsuperscript{1}, Matthias Krause\textsuperscript{1} and Elena Guillén\textsuperscript{2}; Profactor GmbH, Steyr-Gleink, Austria; \textsuperscript{2}Nano4Energy SL, Madrid, Spain.

We present a scalable top-down fabrication method based on nanoimprint lithography (NIL) to be used in the manufacturing of selective solar absorbers. By using a deposition mask, nanodisk arrays are fabricated to create plasmonic metamaterial absorber structures.

The deposition mask is a two-layer system. The underlying lift-off layer aids the subsequent mask lift-off, whereas the NIL fabricated top layer is defining the location and shape where the nanodisks are grown during metal deposition. The chosen pattern layout is not optimized for a solar absorber application, however, due to the versatility of this process, the absorber features could be tailored by choosing an optimized nanopattern for the nanoimprint step.

As proof-of-concept we show the fabrication of elliptical tungsten nanodisks on top of metallic substrates with 100 nm oxide layers, creating a metal nanoparticles-insulator-metal reflector structure. Two different material deposition methods are compared: direct current sputtering and high-power impulse magnetron sputtering. We characterize the fabricated nanodisks by AFM and SEM imaging and comment on the selective absorptivity and thermal stability compared to unstructured absorbers.

4:00 PM *ES08.06.01
Materials Structuring for Enhanced Solar Energy Absorption and Retention

Sungho Jin\textsuperscript{1} and David Wait\textsuperscript{2}; \textsuperscript{1}NanoSD, LLC, San Diego, California, United States; \textsuperscript{2}Solar Reserve, LLC, Santa Monica, California, United States.

Concentrating solar power (CSP) technology has been one of the current renewable electricity generation methods, which has attracted much attention in recent years due to its integration with cost-effective thermal energy storage systems. In order to further reduce the cost of CSP technology, it is imperative to operate the CSP plants at higher temperatures (e.g., \textgreater{}800°C) with enhanced efficiency (e.g., solar-to-thermal figure-of-merit (FOM) as close to the theoretical upper limit of \textasciitilde{}95% as possible), with reduced thermal emission loss. It is also highly desirable to retain or store as much of the absorbed solar energy as possible. In standard CSP tower structures, the metal alloy substrates are considered as geometrically flat, which represents a good IR reflector. However, with specifically designed surface structures such as controlled microcavity or nanocavity array, even the metallic surface can be converted to an excellent solar absorber, especially when combined with a small amount of sunlight-absorbing ceramic coating like the black oxide.

Such unconventional metal surface structures have been prepared which demonstrated very high solar absorptivity values close to 99%, yet exhibited desirable reduced emissivity at high operating temperatures around \textasciitilde{}800°C. These light-trapping micro or nano cavity structures can be fabricated by industrially inexpensive methods. Effects of various structural configurations on light-absorption and emissivity control, and some practical implications will be discussed. Other aspects of solar absorption and desired retention/storage of solar energy will also be discussed.

4:00 PM *ES08.06.02
Preparation and Characterization of Solar Thermal Absorbers by Nanoimprint Lithography and Sputtering

Sungho Jin\textsuperscript{1} and David Wait\textsuperscript{2}; \textsuperscript{1}NanoSD, LLC, San Diego, California, United States; \textsuperscript{2}Solar Reserve, LLC, Santa Monica, California, United States.

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4:15 PM
Fractal-Like Designs for Increased Solar Absorptance and Efficiency of High-Temperature Solar Thermal Receivers

Clifford Ho, Jesus Ortega, Joshua Christian and Julius Yellowhair; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Novel designs to increase light trapping and thermal efficiency of concentrating solar receivers at multiple length scales have been conceived, designed, and tested. The fractal-like geometries and features are introduced at both macro (meters) and meso (millimeters to centimeters) scales. Advantages include increased solar absorptance, reduced thermal emittance, and increased thermal efficiency. Radial and linear structures at the meso (tube shape and geometry) and macro (total receiver geometry and configuration) scales redirect reflected solar radiation toward the interior of the receiver for increased absorptance. Hotter regions within the interior of the receiver can reduce thermal emittance due to reduced local view factors to the environment, and higher concentration ratios can be employed with similar surface irradiances to reduce the effective optical aperture, footprint, and thermal losses. Coupled optical/fluid/thermal models have been developed to evaluate the performance of these designs relative to conventional designs. Modeling results showed that fractal-like structures and geometries can increase the effective solar absorptance by 5 – 20% and the thermal efficiency by several percentage points at both the meso and macro scales, depending on factors such as intrinsic absorptance. Meso-scale prototypes were fabricated using additive manufacturing techniques, and a macro-scale bladed receiver design was fabricated using Inconel 625 tubes. On-sun tests were performed using the solar furnace and solar tower at the National Solar Thermal Test facility. The test results demonstrated enhanced solar absorptance and thermal efficiency of the fractal-like designs.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

4:45 PM CLOSING
* Invited Paper

SESSION ES10.01: Photocatalytic Mechanism  
Session Chairs: Feng Bai, Ying-Bing Jiang and Xinhe Zheng  
Tuesday Morning, April 23, 2019  
PCC North, 100 Level, Room 121 A

10:30 AM *ES10.01.01  
Colloidal Inorganic Nanocrystals with Reduced Symmetry  
P. Davide Cozzoli,
1, 2; 1University del Salento, Lecce, Italy; 2UOS Lecce, CNR NANOyCT - Institute of Nanotechnology, Lecce, Italy.

Colloidal inorganic nanocrystals (NCS), free-standing crystalline nanostructures grown in liquid phase with the aid of surfactants or soft organic templates, stand out in the realm of functional inorganic nanomaterials owing to the precision with which their properties can be controlled through structural and geometric tailoring in the synthesis stage and the flexibility with which they can be exploited in disparate technological fields. A smart, yet challenging paradigm to engineer, differentiate and enrich the physical-chemical prerogatives of NCS relies on designing and creating unconventional architectures, in which diverse compositional, geometric and topological motifs are combined and/or blended across multiple structure and dimensionality levels within reduced-symmetry frameworks. Yet, due to current limitations in synthetic capabilities and related mechanistic knowledge, low-symmetry nanostructures are generally under-represented in the colloidal domain. In this talk I will illustrate progress made by us in the controlled growth and characterization of asymmetric NCS, forged into single-crystalline habits with mixed 1D-2D dimensionality and 2D-3D connectivity, or into multicomponent nanoheterostructures integrating different materials. The technological potential offered by such brand-new NCS will be highlighted.

11:00 AM ES10.01.02  
A Non-Power Strategy for Photo-Generated Charge Carrier Separation—Effect of Lorentz Force in Photocatalytic System  
Wenqiang Gao; Shandong University, Jinan, China.

The promotion of the separation and suppression of the recombination of photo-generated charge carrier have attracted extensive attention in the field of photocatalysis, and constructing heterogeneous junction of photocatalyst by passive types as the core is one of the most effective ways. However, the construction of heterogeneous junction is an uncontrollable and spontaneous process, which may have many disadvantages to improve the photocatalytic performance. In addition, taking advantage of the external fields to enhance charge carrier separation such as electric field enhanced charge carrier separation will bring more energy consumption. Therefore, we proposed a non-power strategy to act on the process of charge carrier transport through Lorentz force and apply in the TiO2 nanobelts to improve the photocatalytic performance. In this work, the results of photoluminescence spectra, photocurrent density and theoretical calculation proved the reaction mechanism that the Lorentz force can effectively promote the separation and inhibit the recombination in the process of the charge carrier transport. It is believed that the new strategy based on the magnetic effect will start a new thinking of the charge separation, and our work will be extremely illuminating to the future researches in the field of photocatalysis.

11:15 AM ES10.01.03  
Isolating Nonthermal Light Effects in Plasmon-Enhanced Catalytic Reactions  
Xueqian Li, Jie Liu and Henry O. Everitt; 1Chemistry, Duke University, Durham, North Carolina, United States; 2Army AMRDEC, Redstone Arsenal, Alabama, United States; 3Physics, Duke University, Durham, North Carolina, United States.

Traditional heterogeneous catalysts that requires high temperatures to overcome reaction barriers often activates undesired side reactions and shortens catalyst lifetimes. The use of illuminated metal nanoparticles in plasmonic photocatalysis has led to accelerated catalytic activities, reduced activation energies, and the ability to select for desired products at reduced temperatures for important chemical reactions. A key challenge in studying such reactions is the separation of the thermal vs. nonthermal contributions. Here, we implement rhodium nanoparticles as a compelling ultraviolet plasmonic photocatalyst for carbon dioxide hydrogenation. Using direct and indirect illumination in conjunction with precise temperature measurements, effects on the overall reactivity of the catalyst from photo-generated hot carriers can be isolated and extracted to reveal the true nonthermal contribution. It is demonstrated that light and heat work together to accelerate important chemical reactions.

11:30 AM ES10.01.04  
Primary Amines Enhance Triplet Energy Transfer from CdSe Nanocrystals for Photon Upconversion  
Emily Moses, Kevin Lee, Jefferson Sun and MingLee Tang; Chemistry, University of California, Riverside, Riverside, California, United States.

Primary amines have been shown to increase the photoluminescence quantum yield (PLQY) of CdSe nanocrystals (NCS), yet little is known about how the binding of amines effects the energy transfer properties of these materials. It is well known that surface effects play the largest role in energy transfer efficiencies in nanocrystalline materials, better understanding, and subsequently controlling surface states is the key to unlocking the full potential of NCS in energy transfer processes, such as upconversion. In this study, CdSe NCS were placed in varying concentrations of 1-propylamine, with and without 2-anthracenecarboxylic acid transmitter ligands attached. This poor transmitter ligand allows for better observation of PL enhancement due to the primary amine. It is shown that adding a primary amine increases the PLQY of the NC, as well as increasing the photon upconversion quantum yield. This effect is maximized at low (11 mM) concentrations of propylamine, while the PLQY can be enhanced further by increasing the amine concentration. By using transient absorption, this work studies the underlying energy transfer processes both enhanced and suppressed by the addition of amine. Through this work the importance of surface trap states are quantified along with the band edge emission of the NC, allowing for a better understanding of important surface chemistry in these complicated systems.

SESSION ES10.02: Self-Assembly and Photocatalysis  
Session Chairs: Yugang Sun, Jiatao Zhang and Xinhe Zheng  
Tuesday Afternoon, April 23, 2019  
PCC North, 100 Level, Room 121 A

1:30 PM *ES10.02.01  
Self-Organized Oxide Nanotubes—Critical Factors in Photocatalytic Applications  
Patrik Schmuki, Ning Liu, JeongEun Yoo and Marco Altomare; Univ of Erlangen-Nuremberg, Erlangen, Germany.

TiO2 nanomaterials have over the last 30 years attracted tremendous scientific and technological interest. Particularly various 1D and highly defined TiO2 morphologies were explored for the replacement of nanoparticle networks and were found in many cases far superior to nanoparticles or their assemblies. Nanotubes or wires can be grown by hydrothermal or template methods, or even more elegantly, by self-organizing anodic oxidation. The latter is not limited to TiO2 but to a full range of other functional oxide structures that on various metals and alloys can be formed. These advanced and doped morphologies can be grown on conductive substrates as ordered layers and therefore can be directly used as functional electrodes (e.g. photo-anodes). The presentation will focus on these highly ordered nanotube arrays of TiO2 (and similar) and discuss most recent progress in synthesis, modification and applications towards photocatalytic and photoelectrochemical applications, such as noble-metal-free H2 generation or the site-selective placement of active centers onto/into these tube layers.

Literature:
Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanoparticles for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, we report the synthesis of such nanoparticles through a surfactant-assisted interfacial self-assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as π-π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanooctahedra, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for potential synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange (MO) pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.


1:00 PM *ES10.02.01 Interfacial Self-Assembly of Hierarchically Structured Nanoparticles with Photocatalytic Activity Hongyou Fan; University of New Mexico/Sandia National Laboratories, Albuquerque, New Mexico, United States.

Gold-palladium (Au-Pd) bimetallic nanoparticles were prepared with a series of alloy and core-shell nanostructures to synergistically couple a plasmonic (Au) and catalytic (Pd) metal to tune their optical and catalytic properties. Catalysts utilizing plasmonic metals that exhibit a localized surface plasmon resonance (LSPR) can be harnessed for light-driven enhancement of small molecule oxidation via augmented carrier generation/separation and photothermal conversion. The colloidal AuPd bimetallic nanoparticles were used as catalysts to study the ethanol (EtOH) photo-oxidation cycle, with an emphasis towards driving carbon-carbon (C-C) bond cleavage at low temperatures. The AuPd nanoparticles were coupled to semiconductor photocatalysts and irradiated with targeted wavelength ranges to probe their effects on plasmonically-assisted photocatalytic oxidation of EtOH. The oxidation of EtOH to CO₂ under solar-simulated-light irradiation was confirmed by monitoring the yield of gaseous products during photo-oxidation experiments using a gas chromatography-mass spectrometry-multiheadspace extraction (GC-MS-MHE) analysis method. The coupling of Au to Pd in an alloy or core-shell nanostructure at higher Au content maintains SPR-induced charge separation, mitigates the carbon monoxide poisoning effects on Pd, and allows for improved hydrocarbon oxidation. Under visible light (>420 nm) irradiation, carrier generation/separation and photothermal conversion was achieved, resulting in the photogenerated “hot” holes driving the photo-oxidation of EtOH, providing a method to selectively cleave C-C bonds. Bimetals provide a pathway for driving desired photocatalytic and photoelectrochemical reactions with superior catalytic activity and selectivity.

1:45 PM ES10.02.04 Hole Transport in Selenium Semiconductors Using Density Functional Theory and Bulk Monte Carlo Atreyo Mukherjee1, Dragica Vasileska2 and Amirhossein Goldan1; 1Electrical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; 2Arizona State University, Tempe, Arizona, United States.

Amorphous semiconductors are useful as they can mimic the properties of their crystalline counterparts while having the ability of being deposited uniformly over a large area at a rapid rate in a thin film geometry. For a great many years, the non-dispersive transport of holes in glassy-amorphous selenium has been of interest. This interest originates from the importance of elemental Selenium as a high-resolution, large-area, wide bandgap, and room-temperature semiconductor with many successful commercial applications such as 2D and 3D medical x-ray imaging. Amorphous selenium is the only amorphous material that undergoes ionization where only holes avalanche at high electric fields and is emerging as a viable large-area imaging detector with avalanche multiplication gain for low-light and low-dose radiation detection applications. This leads to a small Excess Noise Factor which is a very important performance comparison matrix for avalanche photodetectors. Thus, there is a need to model high field avalanche in amorphous selenium. At high fields, the transport in amorphous selenium changes from low values of activated trap-limited drift mobility to higher values of band transport mobility, via extended states. When the transport shifts from activated mobility with high degrees of localization to extended state band transport, then the waveform of the amorphous material resembles that of its crystalline counterpart. Thus, we expect the general details of the extended-state hole-phonon interaction in the amorphous phase to be described by the band-transport lattice theory of its crystalline counterpart’s namely monocrinic and trigonal selenium. To that effect and due to the intrinsic meta-stability of the monocrinic phase and high trap density in prepared specimens, we study hole transport in crystalline trigonal selenium semiconductors using a bulk Monte Carlo technique to solve the semi-classical Boltzmann transport equation (MC-BTE).

In this work we perform molecular dynamic simulations (MD) of vapor-deposited amorphous selenium thin-films using a well-established empirical three-body interatomic potential. On comparing the simulated reduced radial distribution function (RDF) obtained from the MD simulations of amorphous Selenium with monoclinic Selenium and trigonal Selenium, we saw strong correlations over a distance of 10 Å. Thus, we showed that the molecular arrangement for the amorphous phase has considerable local order which may be an explanation for the amorphous general feature of the electronic structure with its crystalline counterparts. Next we utilized density functional theory (DFT) simulations to calculate the density of states and acoustic/optical deformation potentials for the crystalline phases. The accuracy of our DFT model was validated by the very similar results that was previously reported for the ab initio self-consistent energy band structure and previously measured phonon dispersion data for trigonal Selenium. The results from our DFT calculations were then used to calculate the phonon scattering rates which were utilized in the bulk MC algorithm to stochastically interrupt hole free flights. Using our MC-BTE model we calculated phonon-limited low-field drift mobilities which are comparable to published experimental values for trigonal Selenium in both perpendicular and parallel directions to the c-axis for a wide range of temperatures (100-500 k).

To summarize, we showed that holes in selenium can undergo both elastic and inelastic collisions and yet get 'hot', thus gaining more energy from the electric field than they lose to lattice vibrations. This study makes a strong case for the need of a microscopic dynamical model to study hole transport in selenium semiconductor devices.

3:00 PM BREAK

3:30 PM *ES10.02.05 Programmable Assemblies of Inorganic Colloids for Photocatalytic Applications Mikhail Zamkov1, Bowing Green State University, Bowling Green, Ohio, United States.

Colloidal assemblies of complementing nanoscale or molecular components represent a promising class of multifunctional materials. Their composite architecture can allow several reaction steps to progress at the same site with minimal mass and energy transfer distances, which is an important factor for optimizing energy conversion processes in
Nanostructured porous electrodes offer significant advantages for chemical and energy transformations due to their extremely high internal surface area and flexible accommodation of active components, and they have found a wide range of applications including photocatalysis. Their performance is determined by the rate of transport of charge carriers and/or reactants through the porous network as well as their photophysical and chemical properties, however many details remain to be understood. In this talk we will present an analysis of how charge flow and reactant transport are interconnected in a specific type of system, a dye-sensitized solar cell (DSSC) with a 1:1 redox couple, using detailed numerical reaction-diffusion simulations. The DSSC is chosen as a model system for the more general case because a substantial amount of the available literature available on it for model construction and validation. The stochastic, multiscalar computational technique used in this work allows detailed modeling of processes over a very large dynamic range of distances and time, thereby predicting macroscopic observables such as current at the same time as revealing extensive detail about the processes occurring within the porous nanostructured material. The calculations show that at low dye photoexcitation frequencies, the electron distribution in the system and the currents reflect a balance between production of the anode and dye redox cycling that consumes the anode-electrolyte interface in the anode. Electron generation and current flow at high photoexocitation frequencies are controlled by the distribution of the redox electrolyte, which becomes highly nonuniform both in the pores and the electrolyte bulk. Trends in photocatalysis characteristics with pore density and geometry will be described, and some comments on general implications of the DSSC results for other types of systems will be made.


4:15 PM ES10.02.07 Mesoporous Semiconductors—A New Model to Assess Accessible Surface Area and Increased Photocatalytic Activity Alexey S. Cherevan2, Dominik Eder3 and Roland Marschall1, 2 University of Bayreuth, Bayreuth, Germany; 3Technische Universität Wien, Vienna, Austria. Mesoporous photocatalysts have gained great advantage in the last decade by demonstrating that increased surface area and porosity can strongly improve their performance. In fact, all reports on mesoporous semiconductors support this scenario. But is it possible to quantify and compare the reported advantages of the mesopores and the increased surface area between different works? In this contribution, we present a model that can evaluate the improvements in photocatalytic activity achieved by the introduction of mesoporosity independent on synthetic or test conditions. We exemplify this methodology focusing on photocatalytic hydrogen/oxygen evolution with sacrificial reagents, but also include examples of CO2 reduction and electrocatalysis. By correlating the relative increase in surface area to the relative increase in activity – in comparison to non-porous counterparts – we show that the origin of mesoporosity can have a pronounced influence on the activity enhancement, and that different semiconductor materials behave quite differently. Our model can serve as a starting point for the community to extract and compare key photocatalytic data, to put results into context of existing data, and to compare the performances of various catalytic systems much better.


4:30 PM ES10.02.08 Revealing Structure-Activity Relationships in Pt-Functionalized Graphitic Carbon Nitride Photocatalysts Diane Haibet and Peter Crozier; Arizona State University, Tempe, Arizona, United States. Graphitic carbon nitrides (gCNs) offer immense potential as inexpensive photocatalysts for solar fuel generation (e.g., H2 from water) owing to their facile synthesis from a range of precursors, ability to absorb visible light, and high surface area.1 Recent experimental and theoretical work has highlighted the importance of n-type N-H2 defects in facilitating interfacial charge transfer to supported Pt cocatalysts.2 Typically, gCNs are functionalized with Pt via photodeposition at high loadings (e.g., ~1-5 wt%) but recent work has shown that single-atom Pt photocatalyst can also be used for H2 evolution at much lower loadings.2 Nanoscale characterization should reveal more precise structure-function relationships leading to rational design strategies for Pt@gCN photocatalysts that maximize energy conversion efficiency and minimize Pt consumption. A systematic study correlating the hydrogen evolution rates (HERs), bulk characterization of the gCN supports, and Pt dispersion determined from annular dark field scanning transmission electron microscopy (ADF-STEM) was performed to understand photocatalytic activity in Pt@gCNs. Three gCNs demonstrating a range in structural condensation were selected including a commercially-produced “Nicanite” and two urea-derived gCNs. The C/N stoichiometry and bandgap onset energies vary widely with the most structurally condensed gCN (i.e., Nicanite) exhibiting increased visible-light absorption while the least condensed gCN demonstrating moderate structural condensation (i.e., U0.5gCN). The HER of U0.5gCN under visible light is >2x higher than that of Nicanite or U0.5gCN; all were loaded with 1.6 wt% Pt via photodeposition and tested under identical conditions. ADF-STEM imaging of the used Pt@gCN photocatalysts reveals that the Pt dispersion varies widely on each support with U0.5gCN exhibiting the highest Pt dispersion. Moreover, the large Pt nanoparticles and low percentage of Pt photodeposited from solution (i.e., 33% on all supports) widely observed points to an inefficient use of Pt. We find that a photocatalyst containing single-atom Pt, a photocatalyst dispersion with only 0.15 wt% supported on Nicanite can achieve a ~20% greater HER than that of the conventional preparation while reducing Pt consumption by >10x. While promoting, deactivation of the photocatalyst occurred which was attributed to single-atom coarsening. Due to the vast differences in Pt dispersion and visible light absorption among the gCN supports, we argue that the HER (as mass of photocatalyst) is not a suitable metric for photocatalytic activity, although commonly used in this manner. Rather, by normalizing the HER by the total Pt surface area and integrated photon flux above the bandgap onset energy, different gCNs’ photocatalytic activity can be reliably compared. In this view, the order of photocatalytic activity was as follows: U0.5gCN > U0.5gCN > Nicanite. This analysis suggests that “optimal” structural condensation in gCNs should maximize photocatalytic activity whereas both under-/over-polimerization results in poor charge separation/migration. In addition to a discussion of our findings, we will emphasize methods for determining photocatalytic activity and improving the stability of single-atom Pt supported on gCNs.


4:45 PM ES10.02.09 Towards Enhancing Photocatalytic Hydrogen Generation—Which is More Important, Alloy Synergistic Effect or Plasmonic Effect? Zhonghe Xu1 and Dongling Ma2; Shenyang University of Chemical Technology, Shenyang, China; 2University of Quebec, Varennes, Quebec, Canada. Hydrogen generation by solar energy from water splitting is a promising means for replacing traditional fossil fuels. Hitherto, many different tactics have been adopted to improve the efficiency of water splitting. Among them, the use of an alloy structure for achieving synergistic effect and the integration of plasmonic nanostructures for exploiting beneficial plasmonic effect in catalysis appear most promising. In depth understanding and comparison of their respective contributions in certain promising systems is highly desired for catalyst development, yet not investigated so far. We report herein our thorough investigations on a series of highly interesting nanocomposites composed of Pt and Au and C3N4 nanocomponents, which are designed to benefit from both synergistic and plasmonic effects. Detailed analyses led to an important conclusion that the contribution from the synergistic effect was at least 3.5 times that from the plasmonic effect in the best performing sample, Pt3Au25 alloy decorated C3N4. It showed remarkable turnover frequency of >1.6 (mol H2 h-1 kg catalyst)-1 at room temperature. Our work provides physical insights for catalyst development by rationally designing samples to compare long-known synergistic effect with recently emerging, attractive plasmonic effect and represents the first case study in the field.[1]
ES10.03.01

Peering into Water Splitting Mechanism of g-C_{3}N_{4}-Carbon Dots Metal-Free Photocatalyst

Dan Qu and Zaicheng Sun; Beijing Institute of Technology, Beijing, China.

Photocatalytic water splitting is considered one of the promising ways to provide clean fuels. Extensive efforts have been made in the past to develop various inorganic and organic materials systems as photocatalysts for water splitting by using visible light. Among these photocatalysts, it was recently demonstrated that incorporation of carbon dots (CDs) into graphitic carbon nitride (g-C_{3}N_{4}) results in new metal-free composites (gC_{3}N_{4}-C) with excellent stability and impressive performance for photocatalytic water splitting. However, fundamental questions still remain to be addressed such as how added CDs influence the photocatalytic reaction through the bandgap tunability, charge transfer route, and efficiency, as well as the specific function of CDs in the photocatalytic process. Understanding the chemical and physical behaviors of added CDs for the control of gC_{3}N_{4}-C architecture is a critical need for its emergence from the fundamental design of more efficient photocatalysts to practical applications. In this article, we report new materials with well-controlled architecture allowing for fine-tuning band gaps for broader visible light absorption and controlled understanding of the photocatalytic process. The well-defined model materials allow us to address the fundamental question regarding chemically bonding of CDs and how the chemical bonded CDs promote charge separation and transfer for highly efficient generation of H_{2}.

Reference

Qu, Dan; Liu, Juan; Miao, Xiang; Han, Mumei; Zhang, Haochen; Cui, Ze; Sun, Shaorui; Kang, Zhenhui{*}; Fan, Hongyout{*}; Sun, Zaicheng{*}. Applied Catalysis B: Environmental, 2018, 227: 418–424.

ES10.03.02

Orbital Energies Determine Interactivity of Hole Transport Materials with Iodide Species in Degrading Perovskite Devices

Andrew Shapiro1, Ross A. Kerner1, Lianfeng Zhao1, Nakita K. Noel1,2 and Barry P. Rand1,2; 1Electrical Engineering, Princeton University, Princeton, New Jersey, United States; 2Princeton Research Institute for the Science and Technology of Materials, Princeton, New Jersey, United States; 3Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

With improving efficiencies of metal halide perovskite-based photovoltaic and emissive devices, research interest is increasingly focused on understanding and improving device stability. In particular, the effects of mobile ions moving within and escaping from the perovskite material are of interest as they are posited to be a major source of device degradation. While significant research has been conducted on the interactions of these ionic species with the perovskite material as well as the metal contacts of the device, research on the interactions with organic carrier transport or blocking layers is lacking. Using methyliammonium lead triiodide (MAPI) as a prototypical metal halide perovskite, we show that interactions between adjacent organic films with iodine-containing species ejected from the degrading perovskite are significant and material dependent. In the presence of iodine vapor, common small-molecule and polymer hole transport materials (HTMs) are shown to be permeable and susceptible to reversible doping based on their highest occupied molecular orbital (HOMO) energy. Similarly, when in contact with an illuminated MAPI film, the conductivity of the HTM after illumination increases depending on the HOMO level of the material, suggesting iodide doping of the HTM. The strength of the HTM interaction with iodide is found to be linked to the HOMO energy proximity to the iodide/triiodide redox couple energy. Based on these observations, we suggest that the HTM could facilitate perovskite material degradation through loss of iodide, transmit corrosive iodide/triiodide from the perovskite to the device’s metal contacts, and contribute to hysteresis via ionic capacitance from reversible HTM doping. Ultimately, our data bring to light the importance of the HOMO energy and interactivity with respect to the iodide/triiodide redox energy when designing or selecting organic HTMs for perovskite devices.

ES10.03.03

Insight into the Phase Stability of Cesium Lead Iodide Perovskite

Zihan Zhang1, Xi Wang1 and Hanwei Gao1,2; 1Physics, Florida State University, Tallahassee, Florida, United States; 2Condensed Matter Science, National High Magnetic Field Laboratory, Tallahassee, Florida, United States.

As a promising alternative to organo-metal halide perovskite, metal halide perovskite CsPbX (X = Cl, Br, or I) has gathered great research interest because of its better stability against light and heat. Among this kind of perovskite materials, the black-phase CsPbI possesses the optimal bandgap (~1.7 eV) for harvesting solar energy but suffers from the spontaneous phase transition to the photo-inactive yellow-phase in the ambient air at room temperature. In this work, we achieved improved phase stability by confining nanocrystals of black-phase CsPbI in a solid-state matrix. Using microscopic imaging tools, we discovered the correlation between the improved stability and the microscopic morphology of the thin films. Remarkably, the electrical conductivity and photoresponse can be improved simultaneously using this method, indicating its potential for photovoltaic applications.

ES10.03.04

Mixed-Halide Perovskites with Stabilized Blue Emission

Xavier A. Quintana1 and Hanwei Gao1,2; 1Physics, Florida State University, Tallahassee, Florida, United States; 2Condensed Matter Science, National High Magnetic Field Laboratory, Tallahassee, Florida, United States.

The unique bandgap tunability in mixed halide perovskites is desirable for multiple applications such as solar cells, light emitting diodes (LEDs), and sensors. By simply mixing halides ions, the bandgap can be tuned through the entire visible range, such as the blue emission of CsPb(Br,Cl,1-x)I_x. However, suffered from phase segregation, the desired bandgap is not sustainable under operation conditions such as continuous illumination when used in the down conversion LEDs. In this work, we found that the stability of mixed halide CsPb(Br,Cl,1-x)I_x phase is related to the morphology. The morphologically modified mixed halide perovskites exhibited stable photoluminescence peaks with desired wavelengths and narrow bandwidths under extended illumination. Our results demonstrate a facile approach of creating stable halide perovskites with all-inorganic composition and desirable optoelectronic functionalities such as blue LEDs, narrow-band sensors.

ES10.03.05

Reactive Ion Beam Assisted Deposition of Rare Earth Cuprates

Stephen McCoy and Shane Cybart; Materials Science, University of California, Riverside, Riverside, California, United States.

Since the discovery of superconductivity in certain cuprates, these materials have been widely used for research in probing the phenomena of high temperature superconductivity. In particular, YBCO has been extensively studied. To further investigate this material, we have developed and tested a novel approach to growing films of thin films. During reactive sputtering we will introduce a reactive ion source (Reactive Ion Beam Assisted Deposition). We then looking at the transport properties as well as surface morphologies via SEM and AFM and compare film composition and phases with EDX and EBSD. We then make a comparison between reactive ion beam assisted film growth and ion beam assisted samples. We have developed unique single crystal thin films with rare earth series of cuprates containing Holmium and Lanthanum doped YBCO as well as PrBCO and others. We have combined these rare earth series of cuprates onto substrates that have not yet been investigated for rare earth cuprate growth such as NdGaO as well as LaAlO_xSr2TaAlO_y. We have shown transport properties of these materials that further back our claim of thin film single crystal materials.
ES10.03.06
Development of Ozone Gas Sensors Based on Delafossite Thin Films
Joao Afonso; Luxembourg Institute of Science and Technology, Belvaux, Luxembourg.

Ozone gas sensors development is a growing need in modern days, due to its increase use in several industry areas. A major problem is its production in office environment by lab equipments and laser printers. Ozone exposure can cause several long run cardiopulmonary problems. With this in mind there is the urge to develop efficient, cheap and office compatible sensors. Delafossite is an interesting p-type material that has shown its responsibility to ozone. With this in mind we will deeply explore delafossite properties and its responsibility to ozone as well as its integration into devices and understand the underlaying relation. Our delafossite films, are off-stoichiometry Cu$_{1-x}$Cr$_x$O$_2$ These films have interesting electrical properties having proven conductivities up to 100 S/cm. Our films are deposited by Metal Organic Chemical Vapor Deposition (MOCVD) and undergo annealing steps in order to control its electrical properties. These films are compatible with large area deposition and so scalable to industrial processes. We have been developing a state of the art etching process for delafossite with interesting results, leading into the patterning and the integration of the first devices, showing the responsibility to ozone depending on the device geometry.

ES10.03.07
Synthesis of Hydrated KTaWO$_4$ Nanoparticles and Sn(II) Incorporation for Visible Light Absorption
Morton Weiss, Thomas Bredow and Roland Marschall; Justus-Liebig-University Giessen, Giessen, Germany; 2University of Bayreuth, Bayreuth, Germany; 3University of Bonn, Bonn, Germany.

The defect-pyrochlore structured semiconductor KTaWO$_4$ has been prepared via hydrothermal synthesis, resulting in single-crystalline nanoparticles with adjustable crystallite size between 15 and 24 nm.[1] With subsequent ion-exchange of K with Sn(II) the band gap of this complex semiconductor can be reduced by 1.3 eV. We show that the ion-exchange is greatly facilitated by the incorporation of water molecules into the crystal lattice. Moreover, we have systematically investigated the effect of Sn(II) exchange on the band structure and subsequent photocatalytic properties. Different tin precursors show varying influence on the resulting band gap. While the optimum conditions diminish the band gap by up to 1.4 eV, the increase in visible light absorption does not correlate with an increase of photocatalytic activity. The incorporation of Sn(II) may result in smaller band gaps and an increased absorbance of visible light, but this is most likely due to coordination of water or methanol molecules to the incorporated Sn(II) atoms, leading to reduced optical band gaps. This is supported by quantum-chemical calculations of optical spectra.


ES10.03.09
Characterization of TiO$_2$/ZnO Nanocomposite Thin Films on Brass Substrates Prepared by Dip-Coating Process
Kai-Wen Cheng, Yung-Ling Chen and Kun-Dar Li; Material Science, National university of Tainan, Tainan, Taiwan.

In the past decades, the photocatalytic materials that directly convert solar light into chemical energy had been extensively explored for energy and environmental applications. There are some ways used to improve the photocatalytic activity of TiO$_2$, such as doping metal or non-metal ions, or combining TiO$_2$ with another semiconductor. The combination of two semiconductors provides a route to a more efficient charge separation, an increased lifetime of electron-hole pair, and enhanced interfacial charge transfer to absorbed surface of substrates. In this study, we demonstrate a simple method to synthesize TiO$_2$/ZnO nanocomposite thin films on brass substrates. First, TiO$_2$ seed layers are prepared by the sol-gel dip-coating process on brass substrate with a following heat treatment at 500°C for 1 h. Then, TiO$_2$/ZnO nanocomposite thin films with featured morphologies would be formed on the brass substrate. From AES depth profile analysis, it is rationally believed that the diffusion of zinc atoms and reaction with oxygen on the brass substrate surface could be the main mechanism of ZnO formation. As the numbers of coating layers are increased, the (101) peak of TiO$_2$ anatase phase becomes more obvious in XRD analysis and has a small value of FWHM with 0.236 and 0.280 for 5 and 7 layers, respectively. It is also found that the crystallinity of TiO$_2$/ZnO nanocomposite thin films is improved with the increase of film thickness. Furthermore, the photocatalytic activity is evaluated through the degradation efficiency of methyl blue under UV irradiation. In this study, the photocatalytic degradation efficiency of methyl blue for TiO$_2$/ZnO nanocomposite thin films can be achieved more than 46.73%. This investigation has provided a convenient and inexpensive method to synthesize TiO$_2$/ZnO nanocomposite thin films to enhance the development of nanostructures for photocatalytic applications.

ES10.03.10
Alloying Cu and Co with Pt Co-Catalyst Loaded on TiO$_2$ Nanosheets Enhances the Generation of Reactive Oxygen Species and Photocatalytic Degradation
Weixue He and Zhi Zheng; Xuchang Univ, Xuchang, China.

Semiconductor photocatalysis convert solar light to chemical energy represent a promising solution to addressing the current energy and environmental demands. The modification of semiconductor nanomaterials with metallic nanoconponents can promote the separation of electron/hole from photoexcited semiconductors by forming heterojunctions, thus exhibit enhanced photocatalytic activities and potential applications in this study, Pt based NPs, including Pt, PtCu and PtCuCo are employed as model co-catalysts to comparatively study their capability to enhance the photocatalytic activity of TiO$_2$ nanosheets. It was found that each of Pt, PtCu and PtCuCo can greatly enhance the photocatalytic activity of TiO$_2$ toward degradation of organic dyes. Using electron spin resonance spectroscopy, we demonstrated that deposition of Pt based NPs resulted in more production of reactive oxygen species including hydroxyl radicals, superoxide, and singlet oxygen. The enhancing effects of Pt based NPs on generation of ROS and photocatalytic activity showed same trend: PtCuCo > PtCu > Pt. The mechanism underlying the enhancement differences in Pt based NPs may be mainly related to electronic structure change of Pt in alloying with Cu and Co. These results are valuable for designing hybrid nanomaterials with high photocatalytic efficiency for applications in water purification and antibacterial products.

ES10.03.11
Focused Helium Ion Beam Induced Superconductor Insulator Transition in YBCO
Holly Grezdo, Ethan Cho, Hao Li, Jay LeFebvre and Shane Cybart; University of California, Riverside, Riverside, California, United States.

YBCO is a ceramic superconductor discovered in the late 80s with a transition temperature much higher than conventional metal superconductors. It has been difficult to incorporate into electronic applications because of its complexity and difficulty to process. YBCO electronics fabricated utilizing ion beam disorder to directly write electrical patterns show great promise. The key to this method is that modest levels of ion irradiation causes YBCO to change from a metal superconductor to an insulator. Controlling the dose with a finely focused helium ion beam allows for patterning of nanowires and Josephson tunnel devices. The degree of irradiation can be controlled to inflict various levels of damage. As the damage is increased, changes in the normal-state resistivity and temperature dependence can be seen.

We present the superconductor insulator transition as a function of ion irradiation using a helium ion microscope (HIM) to irradiate very thin films of YBCO. To study the junction barrier properties, we use the HIM in the broad beam mode to irradiate a well-defined region. By holding the energy constant, and only varying the dose, we can study the impact at different levels of damage. As the YBCO shifts from superconductor to insulator, the resistivity also changes. To study this effect, we compare and contrast structural materials characterization with electrical transport measurements. Specifically, we measure the resistivity of the irradiated region as a function of temperature and analyze the superconducting transition, normal state resistivity, and temperature independent residual resistivity.

ES10.03.12
Fabrication of ZnO/TiO$_2$ Nanofibers and Their Photocatalytic Activity for Particulate Matter Removal
Chang-Gyu Lee, Kyeonghan Na, Wan-Tae Kim, Dong-Chool Park and Won-Youl Choi; 1Dept. of Advanced Materials Engineering, Gangneung-Wonju National University, Gangneung, Korea (the Republic of); 2WithMtech Co. Ltd., Suwon, Korea (the Republic of); 3Research Institute for Dental Engineering, Gangneung-Wonju National University, Gangneung, Korea (the Republic of).

TiO$_2$ nanomaterials have potential electrical and photochemical applications because of their unique physical and chemical properties. One-dimensional TiO$_2$ nanofibers have been studied in particulate matter (PM) removal applications due to their large specific surface area and high photocatalytic reactivity. To improve the photocatalytic activity, ZnO/TiO$_2$ nanofibers having high adsorption is recently suggested. To fabricate the ZnO/TiO$_2$ nanofibers, electrospinning method which can efficiently produce a nanofiber at low cost was used. The precursor including zinc nitrate hexahydrate, polyvinyl acetate, and titanium isopropoxide was prepared and applied to various electrical fields. The in-
situ ZnO/TiO$_2$ nanofibers were analyzed by Thermogravimetric Analysis (TGA) to get an information of combustion behavior. The rutile phase and diameter of 200 to 300 nm in annealed ZnO/TiO$_2$ nanofibers at 600 were observed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. To analyze the photocatalytic activity in the atmosphere, NO gas was used as a reaction model material. The photochemical reaction rate of 7% was measured by the reaction time, and the photocatalytic activity in ZnO/TiO$_2$ nanofiber were higher than 3% that in TiO$_2$ nanofiber. Photocatalytic properties of ZnO/TiO$_2$ nanofiber will be able to apply to various fields such as moisture separation, environmental purification, super surface, sensor, and disinfection.

**ES10.03.13**

**Dopant Incorporation in Polycrystalline Diamond for PN Junction Fabrication**

Amber Wingfield, Gary L. Harris and Aaron Jackson; Howard University, Washington, District of Columbia, United States.

Diamond, via its extreme properties, presents itself as a material capable of pushing the electronics industry beyond current limitations. It’s ultra-high thermal conductivity, wear resistant, electrically insulating and chemically inertness are just some of diamond’s outstanding properties. Although diamond is an insulator by nature, its wide band gap should allow for incorporation of a variety of donors and acceptors. With an appropriate concentration of either, the material will take on n-type or p-type semiconductor characteristics that can lead to the fabrication of diamond p-n junctions. These p-n junctions have potential application as high temperature and high power operating devices.

In this research, we will detail the characteristics of boron doped p-type and phosphorus doped n-type polycrystalline diamond grown on 6H silicon carbide using a hot-filament chemical vapor deposition system (HF-CVD) in preparation of p-n junction fabrication. Diamond nanoparticles are used to prepare the surface of silicon carbide substrates to enhance nucleation during heteroepitaxial growth. Boron doping is performed by two different methods: 1. In situ during diamond growth via vaporization of solid boron and 2. a pre-deposition followed by a drive in using a boron oxide diffusion source. Phosphorus doping is performed in the same manner as the second method stated using a phosphorus oxide diffusion source. Raman spectroscopy, Hall measurements, and secondary ion mass spectroscopy (SIMS) analysis is conducted to verify diamond quality, active incorporation, and dopant concentrations.

This work is supported by the STC Center for Integrated Quantum Materials, NSF Grant No. DMR-1231319. This work was performed in part at the Harvard University Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. 1541959.

**ES10.03.14**

**Thermal Rectifier in a Melamine Containing Bi-Component Hydrogel**

Ting Meng, Xianjian Wu, Chao Wu, Xiao Zhang, Juekuan Yang, Ping Gu, Jinglei Yang and Yang Zhao; 1; Micro&Nano Thermal Science Lab, University of Science and Technology of China, Hefei, China; 2; University of Science and Technology of China, Hefei, China; 3; Southeast University, Nanjing, China; 4; The Hong Kong University of Science and Technology, Hong Kong, Hong Kong.

Thermal rectifier, which transports heat preferentially in one direction, plays a significant role in thermal circuits. An efficient thermal rectifier should exhibit great different thermal conductivity with the forward and reversed temperature gradient. Thus, the rectifying coefficient defined by the ratio of $k_r$ and $k$. However, the majority of thermal rectifiers show low rectifying coefficient or have a rigorous temperature requirements. In this work, we show an efficient thermal rectifier in a temperature-sensitive hydrogel containing melamine and 6,7-dimethoxy-2,4[(H$_3$H$_3$)]-quinazolinolindone in molar ratio 1:1 at 303K. DSC and rheology results indicate that a thermoreversible first order phase transition occurs when the temperature rises above its upper-critical-solution-temperature (UCST), which can be owned to H-bonding breakage suggested by the Raman-spectra. In this study, the suspended micro-device based on the differential bridge method is applied to measure the thermal conductivity of single hydrogel nanofiber picked out from the dispersion. The thermal conductivity of hydrogel nanofiber reveals an abrupt change with the phase changes. This study provides an efficient realization of a thermal rectifier for heat management that could be implemented in moderate temperature with high rectifying coefficient.

8:30 AM *ES10.04.01*  

**Water Splitting Using Photocatalyst Systems with Hierarchical Structures**

Takashi Hisatomi and Kazunari Domen; Shinsyu University, Nagano, Japan.

Sunlight-driven water splitting has been studied actively for production of renewable solar hydrogen as a storabe and transportable energy carrier [1,2]. Both the efficiency and the scalability of water-splitting systems are important factors because of the low areal density of solar energy. Photocatalyst systems do not involve any secure external electric circuit and thus can be spread over a wide area by inexpensive processes.

The authors’ group has been developing panel-type reactors that can accommodate particulate photocatalysts thinly fixed on substrates [3]. Al-doped SrTiO$_3$ is a photocatalyst that can split water at an apparent quantum yield of up to 69% at 365 nm [4]. Photocatalyst sheets based on Al-doped SrTiO$_3$ contained in a panel-type reactor split water into hydrogen and oxygen and release gas bubbles at a rate corresponding to a solar-to-hydrogen energy conversion efficiency of 10% under intense UV illumination even when the water depth is merely 1 mm. Moreover, it is possible to maintain the intrinsic activity of the photocatalyst sheets when the size of the panel is extended to the scale of 1 m$^2$. It is likely feasible to build panel-type photocatalytic reactors suitable for scale-up using lightweight materials inexpensively. Accordingly, development of photocatalyst systems that can split water under visible light irradiation efficiently is a key issue of the research field.

We have developed particulate photocatalyst sheets consisting of hydrogen evolution photocatalysts (HEPs) and oxygen evolution photocatalysts (OEPs) embedded into conductive layers by particle transfer [5-9]. The photocatalyst sheet shows significantly higher water splitting activity than the corresponding powder suspension systems, because conductive matrices transfer photogenerated electrons between HEP and OEP particles effectively. In addition, evolution of hydrogen and oxygen in close proximity prevents generation of the pH gradient during the water splitting reaction. Therefore, the photocatalyst sheet is scalable without sacrificing the high activity. A photocatalyst sheet consisting of La- and Rh-codoped SrTiO$_3$ as the HEP and Mo-doped BiVO$_4$ as the OEP embedded into a carbon conductor exhibits a solar-to-hydrogen energy conversion efficiency of 1.0% at ambient pressure [8]. Photocatalyst sheets can also be prepared by ambient-pressure processes, namely by screen-printing photocatalyst ink containing transparent conductive oxide colloids [9].

It has been known that Ta$_x$N$_y$ has a band structure suitable for water splitting under visible irradiation of up to 600 nm since 2002 [10,11], but overall water splitting had not been achieved because of high densities of trap states. We have activated Ta$_x$N$_y$ in overall water splitting under visible light by developing an innovative nitrlation process [12]. Ta$_x$N$_y$ single crystal nanorods can be directly evolved on particulate KTaO$_3$ by short-time nitrlation accompanied by gradual evaporation of K contents. Ta$_x$N$_y$ single crystal nanorods have low defect densities and can utilize photoexcited carriers in the water splitting reaction when being loaded with appropriate cocatalysts.

In this talk, development of photocatalyst systems involving hierarchical structures will be presented.

Semiconductor Electrodes for Integrated Photo-Electrochemical Water Splitting Lianzhou Wang; University of Queensland, St Lucia Brisbane, Queensland, Australia.

Semiconductor materials hold the key for efficient photocatalytic and photoelectrochemical water splitting. In this talk, we will give a brief overview of our recent progresses in designing semiconductor nanomaterials for photoelectrochemical energy conversion including photocatalytic solar fuel generation. In more details, we have been focusing the following a few aspects; 1) band-gap engineering of layered semiconductor compounds including layered titanate, tantalate and niobate-based metal oxide compounds for visible light photocatalysis, and 2) two-dimensional nanosheets/nanoplates of TiO\textsubscript{2}, Fe\textsubscript{3}O\textsubscript{4}, WO\textsubscript{3}, BiVO\textsubscript{4} as building blocks for new photoelectrode design, and 3) the combination of a high performance photocatalyst BiVO\textsubscript{4} with perovskite solar cells can lead to unassisted solar driven water splitting process with solar-to-hydrogen conversion efficiency of >6.5%.\textsuperscript{1,4} The resultant material systems exhibited efficient visible light photocatalytic performance and improved power conversion efficiency in solar energy, which underpin important solar-energy conversion applications including solar fuel generation and simultaneous environmental application.

9:30 AM *ES10.04.03
Studying Photo-Induced Charge Transfer with Quantum Dots and Molecular Catalysts Assembly for Photocatalytic Applications Nihaarika Krishna Botcha, RR Gutha, SM Sadeghi and Anusree Mukherjee; The University of Alabama in Huntsville, Huntsville, Alabama, United States.

Photocatalytic water splitting using solar energy for hydrogen production offers a promising alternative form of storable and clean energy for the future. Light driven proton reduction requires a three-component system with a photosensitizer (light harvesting unit) that transfers electrons to a catalyst that reduces protons and a sacrificial donor. To make this process cost-effective, we need an inexpensive, durable and efficient catalyst that is capable of reducing protons from water to produce hydrogen and we need to couple this catalyst to a photosensitizer that could supply the energy required for water splitting.

Quantum dots (QDs) have high extinction coefficients across a broad range in the solar spectrum and can simultaneously absorb multiple photons, or continuously absorb multiple photons even after the electrons and holes are accumulated. These characteristics make QD the perfect candidates for photosensitizers in solar fuel generation when they are properly coupled to efficient catalyst for hydrogen generation.

Nature provides an attractive inspiration for the reductive cycle of water splitting in the form of hydrogenases using earth abundant and inexpensive transition metals in the active site. Transition metals are useful because of their redox activity, their capability to bind and exchange ligands and their high charge density. As a result, many homogeneous catalytic systems incorporate transition metals.

The fundamental step for photocatalysis is to generate a charge separated state. In order to couple a catalyst for proton reduction to a photosensitizer, it is essential to understand the mechanism of charge transfer or photoinduced electron transfer from the photosensitizer to the catalyst. Hence our work is focused on the study of light driven production of hydrogen from QD systems by modification with reduction catalysts. We synthesized and characterized a variety of nickel and copper complexes of tetradeutate ligands with amine and pyridine functionalities (N\textsubscript{2}/Py\textsubscript{2}) and studied their interactions with Cadmium Telluride QDs stabilized by 3-mercaptopropionic acid (MPA-CdTe QDs). The studies performed include absorbance and emission spectroscopic behavior as well as lifetime measurements that will give us a direct insight into the photo-induced charge transfer process.

9:45 AM ES10.04.04
Self-Optimized Photocatalysts—Hot-Electron Driven Selective Photo-Synthesis of Catalytic Nanoparticles Evgenia Kontoleti, Sven Askes and Erik Garnett; AMOLF Institute, Amsterdam, Netherlands.

It is well known that plasmonic gold nanostructures feature extraordinary capability of absorbing visible light and concentrating the excitation energy in subwavelength volumes. Recently, they have also been applied for catalyst production for the production of chemical fuels from sunlight. Upon excitation of these nanostructures, the energy is transferred to single electrons that for a brief period of time become highly energetic. Recent scientific advances demonstrate that these highly energetic, “hot” electrons can be extracted and used to drive chemical reactions, such as the conversion of protons to molecular hydrogen. However, to greatly improve the production rate, expensive and rare cocatalysts such as platinum are required.

In order to make effective use of as little catalyst material as possible, it is therefore important to localize the cocatalyst at the places where it is best coupled to the photogenerated hot electrons. To this end, we use the hot electrons themselves to deposit the cocatalyst and to construct photocatalytically active nanostructures. Briefly, a photocathode consisting of ITO-gold nanoslands-TiO\textsubscript{2} was illuminated with red light in presence of PtCl\textsubscript{6}\textsuperscript{4-}, which resulted in the local deposition of platinum nanoparticles on the gold nanoslands. We furthermore compare the photocatalytic performance of these photocathodes, where the platinum nanoparticles were selectively deposited, with those that were fabricated by a random-deposition technique, i.e. electrodeposition. Indeed, the samples where the cocatalyst was locally-deposited, with hot-electron chemistry, showed higher catalytic activity in photocurrent measurements in presence of a phosphate buffer. Therefore, it seems that indeed the location of the cocatalytic material on the plasmonic photocathodes, and maybe generally on photoactive materials, plays a crucial role.

Overall, these results demonstrate that plasmonic hot electron chemistry can be used for fabricating photocatalytic nanostructures with sub-wavelength control over localization. This careful design of photoelectrodes with nanoscale precision, could open up a new way for higher photocatalytic efficiencies as well as lower fabrication costs.

References
1. Z. Zhao, and Z. Sun et al., Sci. China Mater., 2018, 10.1007/s40843-017-9170-6

Photocatalytic water splitting and CO\textsubscript{2} reduction are attractive reactions to convert photon energy to chemical energy, and hence they are called as artificial photosynthesis. The...
photocatalyst systems for water splitting and CO\(_2\) reduction can be divided into powdered and photoelectrode types. In both types, photogenerated electrons have to migrate to photocatalyst particles to other particles or conductive substrates. In the present study, we successfully developed new photocatalyst systems for water splitting and CO\(_2\) reduction upon combining photocatalysts and a conductive reduced graphene oxide (RGO).

In a powder-based photoelectrode system in which the photocatalyst particles are loaded on a conductive substrate, photogenerated carriers in a particle need to migrate to the conductive substrate through other particles. We found that the photoelectrochemical performance is improved upon incorporating the RGO in the photoelectrode due to the boosted electron transfer from the particles to the substrate by the RGO. The incorporation of the RGO was effective for both n- and p-type semiconductor materials.

A powdered Z-scheme system consists of two different photocatalysts and an electron mediator. Although ionic redox couples are usually used as the electron mediator, we found that the RGO works as a solid-state electron mediator. Additionally, we successfully utilized photocorrosive metal sulfides as an H\(_2\)-evolving photocatalyst when the RGO was used. The developed Z-scheme system showed the activity for CO\(_2\) reduction as well as water splitting under visible light irradiation.

11:30 AM ES10.04.07
Janus-Type MnO\(_x\)-Ag\(_x\) Nanoparticles as Self-Sensitized Photochemical Water Oxidation
Jie He; University of Connecticut, Storrs, Connecticut, United States.

Janus nanoparticles (NPs) containing two chemically distinct materials in one system are of great significance in nanocatalysis in terms of harnessing catalytic synergies that are not exist in either component. We herein present a novel synthetic method of Janus-type MnO\(_x\)-Ag\(_x\) NPs consisting of n-type MnO octahedrons and p-type Ag NPs for efficient photocatalytic water oxidation. The synthesis of Janus-type MnO\(_x\)-Ag\(_x\) NPs is based on the oxidative nucleation and growth of Ag domains on MnO first and the subsequent iodization of Ag. A mild, non-disruptive iodization strategy is developed to yield Janus MnO\(_x\)-Ag\(_x\) NPs in which converting Ag to AgI domains with iodomethane (CH\(_3\)I) is achieved through the partial iodization. Simultaneously, Mn\(^{2+}\) species in the primary MnO octahedrons are oxidized during the growth of Ag NPs, leading to the formation of n-type MnO\(_x\) domains. Therefore, as-resultant Janus-type MnO\(_x\)-Ag\(_x\) NPs combining two semiconductors into an integrated nanostructure can be used as an efficient self-sensitized photocatalyst for visible light-driven water oxidation. Janus MnO\(_x\)-Ag\(_x\) NPs show a superior photocatalytic activity (358 mmol O\(_2\) per mg\(_{\text{catalyst}}\) in 4 min) even in the absence of [Ru(bpy)]\(^{3+}\) as a photosensitizer. This intriguing synthesis may open up a new opportunity to develop silver halide asymmetric nanostructures that will potentially be efficient photocatalysts for solar-driven water splitting.

11:45 AM ES10.04.08
Comparing Catalyst-Mass-Normalized Activity and Approximated Quantum Yields for Polychromatic Photocatalytic Systems
Larissa Y. Kunz, Anan Majumdar and Matteo Cargnello; Stanford University, Stanford, California, United States.

In spite of the potential of using photocatalysts to sustainably produce fuels and chemicals, overall reaction rates remain prohibitively low, limited by recombination of photogenerated electrons and holes. Extensive work can be found in the literature on suppressing this recombination by addition of co-catalysts. However, much of the reported data on photocatalytic activity are rendered ineffectual in the rational design of new, improved catalyst systems by the common practice of reporting activity on a catalyst mass basis. In this work, using a model system of TiO\(_2\) and g-C\(_3\)N\(_4\) with Pt, we show that normalizing photocatalytic rates by mass is non-physical and can even artificially enhance the apparent performance of a two-photosabsorber system relative to that of the individual components. A mathematical method is presented for approximating a system’s quantum yield from measured reaction rates under simulated solar or otherwise polychromatic light. A sensitivity analysis was performed on this method, demonstrating how the approximated quantum yield can be used to evaluate the degree of relative enhancement introduced by mass-normalizing photocatalytic reaction rates for any set of photosabsorbing co-catalysts.

SESSION ES10.05: Photocatalytic Water Splitting II
Session Chairs: Jian Zhang and Jiatao Zhang
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 121 A

2:00 PM *ES10.05.01
Cocatalysts Decorated Amorphous Silicon Photoanodes for Efficient Bias-Free Water Splitting
Jian Zhang; Guilin University of Electronic Technology, Guilin, China.

Silicon materials have many advantages, including earth-wide, wide spectra absorption, high solar to chemicals conversion efficiency, suitable band edge. However, the amorphous silicon-based photoelectrode is very easily to be corroded by electrolyte. In the presentation, cobalt oxide by magnetron sputtering at ambient temperature was introduced as a protective layer in water oxidation, and atomic Pt as HER cocatalysts prepared by magnetron sputtering method on thin film silicon was used for water reduction. The photoanode delivered a current density of 7.3 mA cm\(^{-2}\) at 1.23 V vs. RHE, and the onset potential was negative shift to 0.62 V. The photocathode current density at the 0 V vs RHE was increased to 12.03 mA cm\(^{-2}\) in 1M KOH electrolyte with the onset potential of 0.82 V. The Pt/Si faradic efficiency was ~100% and the fill factor was 38% that was the highest value among Si-based PEC system. Pt and CoO\(_2\) strengthened the inner electric field and passivated the surface of photoelectrodes. The dual-amorphous silicon photoelectrodes integrated CoO\(_2\) and Pt realized the bias-free water splitting at 0.81 V with a photocurrent of 1.5 mA cm\(^{-2}\) and 0.92 % of the solar to hydrogen efficiency. The novel amorphous silicon photoanode provides a promising strategy for photo-electrochemical energy conversion and storage.

Acknowledgement: This research was financially supported by the National Natural Science Foundation of China (61564003, 61774050), and the Guangxi Natural Science Foundation (2015GXNSFGA139002), and the Guangxi Bagui Scholar program.

References (12 pt)
- C. Xu, Y. Hu*, Z. Zhang, Y. Sheng, P. Jiang, H. Han, J. Zhang,* submitted.

2:30 PM BREAK

3:30 PM *ES10.05.02
Plasmonic Driving of Chemical Reactions
Jianfang Wang; Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong.

Plasmonic metal nanocrystals can interact strongly with light, efficiently converting light into heat and generating hot carrier charges. Both plasmonic photothermal conversion and hot carrier generation can accelerate chemical reactions. The use of plasmons to drive chemical reactions has recently become a new and active research field. Plasmonic hot charge carriers can not only enhance the reaction yield and selectivity, but also introduce new reaction pathways.

The lifetime of plasmonic hot charge carriers is on the femtosecond scale. Without immediate usage, they will rapidly relax, converting their energy into heat. We have employed two approaches to enable the use of plasmonic hot charge carriers. The first is the integration of Au or Ag nanoparticles with Pt or Pt nanoparticles. Au and Ag nanoparticles possess strong localized plasmons, while Pt and Pt nanoparticles are excellent catalysts for many chemical reactions. Combination of the two types of metal nanoparticles can lead to efficient light absorption and generation of plasmonic hot charge carriers, which can subsequently inject into molecules that are adsorbed on the Pt or Pt component. We have applied this approach to enhance Suzuki coupling reactions by localized plasmons.
The second is the integration of plasmonic metals with semiconductors. A barrier is formed at the interface. The generated hot electrons and holes can quickly inject into the bandgap or valence band and therefore get separated. The injected charge carriers can then drive chemical reactions. We have synthesized Au/ TiO\textsubscript{2}, Au/CoO; and Au/ BiOCl hybrid structures as plasmonic photocatalysts to drive the photo-generation of reactive oxygen species, the selective oxidation of alcohols, and N\textsubscript{2} photofixation. Specifically, oxygen vacancies have been introduced in the metal oxides to “work in-tandem” together with plasmonic hot charge carriers. For example, during the use of Au/BiOCl hybrid structures for the photocatalytic selective oxidation of benzyl alcohol, oxygen vacancies on BiOCl facilitate the trapping and transfer of plasmonic hot electrons to adsorbed O\textsubscript{2}, producing superoxide anion radicals, while plasmonic hot holes remaining on the Au surface mildly oxidize benzyl alcohol to corresponding carbon-centered radicals. The ring addition between these two radical species leads to the production of benzaldehyde along with an unexpected oxygen atom transfer from O\textsubscript{2} to the product. In contrast, the oxygen atom in the product is from the benzyl alcohol reactant.

In another example, Au nanoparticles are anchored on ultrathin TiO\textsubscript{2} nanosheets with oxygen vacancies. The oxygen vacancies on the nanosheets chemisorb and activate N\textsubscript{2} molecules, which are subsequently reduced to ammonia by hot electrons generated from plasmon excitation of the Au nanoparticles. The hybrid photocatalyst can accomplish photodriven N\textsubscript{2} fixation in the “working-in-tandem” pathway at room temperature and atmospheric pressure. The apparent quantum efficiency of 0.82% at 550 nm for the conversion of incident photons to ammonia is higher than those reported so far. The oxygen vacancies play three roles. They act as the active sites for N\textsubscript{2} molecules; they cause defect states within the bandgap for trapping plasmonic hot electrons and therefore lengthening their lifetime; and they function as a bridge between plasmonic hot electrons and the activated N\textsubscript{2} molecules. This work offers a new approach for the rational design of efficient catalysts towards sustainable N\textsubscript{2} fixation through a less energy-demanding photocatalytic process compared to the industrial Haber-Bosch process.

4:00 PM ES10.05.03
Silicon Photocathodes with Integrated Catalysts Perform Selective CO\textsubscript{2} Reduction to Hydrocarbons and Oxygenates
Gurunavlaj Gurunavala\textsuperscript{1, 2} and Joel W. Ager\textsuperscript{1, 2}; 1Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2School of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Photocathodic (PEC) devices combine light capture, charge separation, and electrocatalysis to drive solar to chemical energy conversion. Silicon based photocathodes integrated with co-catalysts have been studied extensively for solar fuels production, especially for the hydrogen evolution reaction of PEC water splitting. In contrast, Si photocathodes that drive the more challenging CO\textsubscript{2} reduction (CO\textsubscript{2}R) reaction are fewer in number and, with only a few exceptions, produce 2 electron products such as CO or formate.\textsuperscript{2} Here we show that Si photocathodes integrated with nanostructured bimetallic catalysts perform light-driven conversion of CO\textsubscript{2} to C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{5}OH products. In contrast to conventional photocathode designs which employ p-type absorbers, we employ a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Surface texturing of the Si was used optimize light absorption on the illuminated side and increase the surface area available for catalysis on the electrolyte side. Based on our prior work with bimetallic cascade catalysis,\textsuperscript{3} we employed a hierarchical Au-Cu or Ag-Cu nanostructures to drive CO\textsubscript{2}R to C-C coupled products.

The photovoltaic, 550-600 mV under simulated 1-sun illumination, confirms the carrier selectivity and passivation of the front and back interfaces. Compared to planar controls, textured photocathodes generate higher current densities, exceeding 30 mA/cm\textsuperscript{2}. Under simulated diurnal illumination conditions in CO\textsubscript{2}-saturated 0.1 M CsHCO\textsubscript{3} electrolyte, over 60% faradic efficiency to C\textsubscript{2}- hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. Over longer testing periods, contamination from the counter electrode is observed, which causes an increase in hydrogen production. This effect is mitigated by a regeneration procedure which restores the original catalyst selectivity. A tandem, self-powered CO\textsubscript{2}R reduction device was also demonstrated by coupling a Si photocathode with two series-connected semitransparent CH\textsubscript{3}NH\textsubscript{2}PbI\textsubscript{3} perovskite solar cells, achieving an efficiency for the conversion of sunlight to hydrocarbons and oxygenates of 1.5% (3.5% for all products).


4:15 PM ES10.05.04
Photocatalytic Hydrogen Generation in CdSe Quantum Dot–Pb\textsubscript{1.1}Pb\textsubscript{0.9}V\textsubscript{2}O\textsubscript{5} Nanowire Heterostructures, Mediated by Midgap States
Junsang Cho\textsuperscript{1, 2}; Sarbajit Banerjee\textsuperscript{3} and David Watson\textsuperscript{1}; 1Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, United States; 2Chemistry, Texas A&M University, College Station, Texas, United States; 3Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

We are integrating theory and experiment to design, synthesize, and characterize semiconductor heterostructures with programmable light harvesting and charge transfer for photocatalysis. Heterostructures consist of M\textsubscript{V\textsubscript{2}}O\textsubscript{5} nanowires (NWs), where M is an intercalated metal cation, interfaced with quantum dots (QDs). Intercalation of metal cations gives rise to midgap electronic states in the NWs, which are well-positioned to accept photogenerated holes from QDs, facilitating charge separation and redox photocatalysis. We previously demonstrated that photocatalysis of cadmium chalcogenide QDs, within heterostructures, is followed by the transfer of holes to midgap states of NWs on sub-picosecond time scales.\textsuperscript{1} This presentation will focus on recent research to evaluate the heterostructures in photoelectrochemical hydrogen evolution and photocatalytic water splitting. Photoelectrochemical measurements revealed that CdSe/Pb\textsubscript{1.1}Pb\textsubscript{0.9}V\textsubscript{2}O\textsubscript{5} heterostructures exhibited (3.2 ± 0.4)-fold greater photocurrents than corresponding CdSe/V\textsubscript{2}O\textsubscript{5} heterostructures (where the V\textsubscript{2}O\textsubscript{5} NWs lack midgap states) following selective excitation of CdSe QDs and (5.7 ± 0.3)-fold greater photocurrents under white-light illumination. Photocurrents arose from the reduction of aqueous H\textsuperscript{+} to H\textsubscript{2} with high Faradic efficiencies of 92% ± 5% in 0.33 M sulfuric acid solution. These results are consistent with a mechanism in which excited-state interfacial hole transfer facilitates charge separation and photocatalysis, and suggest that the CdSe/Pb\textsubscript{1.1}Pb\textsubscript{0.9}V\textsubscript{2}O\textsubscript{5} heterostructures are indeed promising architectures for light harvesting and photoelectrochemical water splitting. This presentation will highlight these results, as well as recent experiments on second-generation heterostructures with optimized interfacial energetics.

(1). Millerville, C. C.; Pelcher, K. E.; Stefr, M. Y.; Banerjee, S.; Watson, D. F.: Directional charge transfer mediated by midgap states: A transient absorption spectroscopy study of CdSe quantum dot–Pb\textsubscript{1.1}Pb\textsubscript{0.9}V\textsubscript{2}O\textsubscript{5} heterostructures. The Journal of Physical Chemistry C 2016, 120, 5221-5232.

4:30 PM ES10.05.05
The Optical Spectrum of UVLED Excitation Using NTC Nanometer Particulate Exchange to Replace Rare Earth Doping
Lihong Su\textsuperscript{1}; Kan Chen\textsuperscript{1}; Yongqiang Liu\textsuperscript{1}; Ziao Zou\textsuperscript{1}; Lihua Su\textsuperscript{2} and Juancheng Wang\textsuperscript{3}; 1Northwest Polytechnical University, Xi'an, China; 2Shaanxi Zoomview Company, Xi'an, China; 3University of Southampton, Southampton, United Kingdom; 4Xi'an Communicate Institute, Xi'an, China.

Ultraviolet light-emitting diodes (UVLEDs) with phosphor materials have considerable advantages over traditional illumination devices. Doping with rare earth ions can modify the optical spectrum of phosphor materials, but rare earths are very expensive. Thus, replacing rare earths with a common material would provide a great potential for the wide application in the future. In this study, we discovered that a novel type of semiconductor nanometer powder, namely manganese cobalt nickel copper oxide (MCNC), is able to emit blue-green wavelength spectrum when excited by 365–400nmUVLED. In addition, MCNC shows less attenuation of luminescence efficiency than other UVLED phosphor materials doped with rare earths with temperature increase. It is thus concluded that MCNC is a promising low-cost material to replace rare earths to adjust the optical spectrum wavelength of UVLED. This is the first time that nano-scale MCNC is reported to change the optical spectrum wavelength of UVLED. This provides a new mechanical and nanometer phosphor material without rare earth doping to shift the wavelength spectrum.
Plasmonic materials have attracted much attention owing to their unique surface plasmon effect (SPP) by photoluminescence. As a typical anisotropic plasmonic material, gold nanorods (GNRs) have advantages of good biocompatibility, adjustable light response between 550 - 1550 nm and high chemical stability. In recent years, studies show gold nanorods can enhance the photocatalytic activity of semiconductor materials, but most of the inorganic semiconductors are used for photocatalysis which absorb spectrum lies in ultraviolet region. In order to improve the utilization of visible light, efficient photocatalysts with visible light responsive need to be designed and prepared. Porphyrin assembly is an organic semiconductor material with excellent photoelectric properties. Compared with traditional inorganic semiconductor materials such as TiO$_2$, the absorption spectrum of the porphyrin is located in the visible light region, which can make use of solar energy more effectively, but Pt must be added as co-catalyst. Therefore, the paper chooses gold nanorods and porphyrin assemblies to make a composite, in order to make use of more efficient solar energy utilization materials. Here, we synthesized a gold nanorods-porphyrin core-shell structure via a surfactant-assisted self-assembly induced acid-base neutralization micelle encapsulation method. The fabrication of composite was achieved by adjusting the length diameter ratio of GNRs, the type and concentration of surfactants, and pH. By regulating the reaction parameters, the composite structure with regular morphology, uniform size and good monodispersibility was prepared by using CTAB/NaOH coated GNRs with a length/diameter ratio greater than 4. Combined with TEM and the dynamic tracking experiment indicated the composite structure was the core-shell structure of porphyrin assemblies covering GNRs. The XRD result showed the GNRs-ZnPpy core-shell structure had good lattice structure. The photocurrent test showed that the photocurrent density of GNRs-ZnPpy-core-shell structure and ZnPpy core-assemblies was about 2.0 μA/cm$^2$ and 0.8 μA/cm$^2$ respectively, and the core-shell structure was 2.5 times as high as that of self-assemblies. Using ascorbic acid (AA) as electron donor, the visible light photocatalytic hydrogen production without Pt of different catalyst systems were carried out under pH ≈ 5.0. Under the same condition, the GNRs-ZnPpy core-shell structure had a H$_2$ production rate of 37 nmol/g, which was 15 times of the physical mixing.

**ES10.06.02**
Ultra Small Metal Oxide/Phosphide Clusters Anchored on TiO$_2$ Nano-Sheets Remarkably Enhance Photocatalytic H$_2$ Generation Yun Gao, Xiao Luo, Yuwen Bao and Jingting Si; Hubei University, Wuhan, China.

Converting solar energy into hydrogen fuels through photocatalytic water splitting is a promising way for solving the energetic and environmental problems. The development of an efficient, robust, low cost and noble-metal-free catalyst for H$_2$ evolution is of great importance for both scientific research and technological application. Downscaling the co-catalyst particles to sub-nano clusters and even single atom helps to enlarge the active sites and thus dramatically improves the H$_2$ generation. Therefore, it is important to develop a general method to synthesize the sub-nano cluster co-catalysts. In this presentation, we report the synthesis of sub-nanometer Fe, Co, Ni oxide and phosphide as co-catalysts anchored on the 2D ultrathin TiO$_2$ nanosheets by a facile two-step hydrothermal method. The 2D ultrathin TiO$_2$(B) nanosheets are prepared firstly by a hydrothermal method. In the second step, the prepared TiO$_2$(B) nanosheets are added into the solution as the nucleate substrate for the formation of transition metal oxide and phosphide. The microstructures of the samples are examined by HAADF-STEM performed on a JEOL JEM-ARF200F. In the water splitting measurement, 20% methanol aqueous solution is used as the hole sacrificial agent, and the generated hydrogen production is sampled and analyzed by gas chromatography (GC-2018, Shimadzu, Japan, TCD). The energy band structure at the interface of the hybrid catalysts is analyzed to understand the H$_2$ generation mechanism. It is found that, the cluster sizes of transition metal oxide and phosphide anchored on the surface of TiO$_2$ nanosheets are drastically reduced to sub-nanomter range, while their counterpart products without adding TiO$_2$(B) nanosheets keep the size larger than tens nanometers. A remarkably enhanced and highly stable photocatalytic activity is obtained by using the hybrid composite catalysts. In addition, the photocatalytic activity is affected by the PH value in the water splitting process. As the size of transition metal oxide and phosphide is reduced to certain scale by carefully adjusting the hydrothermal reaction condition, the maximum photocatalytic activity of the composite catalysts could exceed that using Pt cluster as the co-catalysts. When metal oxide is used as co-catalyst, the charge transfers from TiO$_2$ to the co-catalyst, reducing the oxide into metallic cluster, and thus enhances the photocatalytic activity. On the other hand, metal phosphide clusters act as the active site and accept the photo-generated electrons transferred from the conduction band of TiO$_2$. This leads to a significant improvement of the H$_2$ generation efficiency. In conclusion, the 2D ultrathin TiO$_2$(B) nanosheets with huge specific surface area and abundant surface defects provide plenty of effective scaffold and nucleation sites for the Fe, Co, Ni metal oxide and phosphide to nucleate and firmly anchor on the surface of TiO$_2$(B) nanosheets. The stable nucleation interface not only provides a high efficient charge separation and transfer route, but also helps to maintain the microstructure of the composite catalysts and keep the long term stability of the H$_2$ generation efficiency. The composite catalysts developed in this work can be used to replace and indeed out-perform noble metals, such as Pt, as effective and stable H$_2$ evolution co-catalysts.

**ES10.06.03**
Controlling Stoichiometry and Morphology in Tin-Halide Perovskite Films Deposited by Carrier-Gas Assisted Vapor Deposition Catherine P. Clark; Ersay S. Aydil and Russell J. Holmes; 'Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States; 'Tandon School of Engineering, New York University, Brooklyn, New York, United States.

Carrier-gas assisted vapor deposition (CGAVD) is used to systematically control the growth of CH$_3$NH$_3$SnBr$_3$ thin films across a wide range of stoichiometries and morphologies. Our home-built CGAVD system enables more precise morphological control as compared to high-vacuum physical vapor deposition methods, as well as the ability to grow multi-layered perovskite stacks which are typically inaccessible using solution processing. Here, tin-halide perovskite films are grown via co-deposition of CH$_3$NH$_3$X and SnX$_2$ (X = I, Br), where each component vapor is carried from a hot source to a cool substrate by means of a N$_2$ carrier gas stream. CGAVD offers a broad selection of processing parameters, allowing us to tailor stoichiometry, grain size and film texture. Chief among these are the source material temperature (T$_{source}$ = 140 °C – 290 °C), carrier gas flow rate (V$_{flow}$ = 2 sccm – 100 sccm), substrate temperature (T$_{sub}$ = 8 °C – 40 °C), and chamber pressure (P = 350 mTorr – 10 Torr). In varying these parameters, we have realized corresponding changes in grain orientation and grain size from ~100 nm to over 1 µm. Moreover, the morphologies accessed using this technique are consistent across many substrates, including quartz, silicon, ITO, CaTiO$_3$, and PEDOT:PSS, allowing facile integration of CGAVD films into different device-relevant architectures while maintaining the same morphology. Having established optimized deposition conditions for CH$_3$NH$_3$SnBr$_3$, CGAVD can be applied to other halide perovskite systems to enable growth of previously inaccessible morphologies and multi-layer perovskite structures.

**ES10.06.04**
Defect Chemistry-Inspired Design of Ir$^{3+}$/FeO$_2$ Single-Atom Catalyst for Water Splitting Photoanode Wonho Joo; Hyoung Gyun Kim; Ho-Young Kang; Mi-Young Kim and Young-Chang Joo; 'Seoul National University, Seoul, Moldova (the Republic of); 'LG Chem Ltd., Seoul, Korea (the Republic of).

Single-atom catalysts where active metal atom is dispersed on the surface of the support have received great attention due to their high specific activity and unique selectivity. It is well known that single-atom is anchored on the defect site of the catalyst. However, there has been little effort to correlate the number and type of defects and the resultant catalytic activity. Hematite is one of the most prominent photoelectrochemical catalysts for water oxidation reaction, in virtue of its good optical property and cost-effectiveness. However, its widespread adaptation to commercial usage has been limited due to its modest charge transport property and poor surface reaction kinetics. To overcome these, in this work, the concept of single atom catalyst is applied and the contribution of defect to the catalytic activity is investigated. Hematite is defect chemically modified by atmosphere change and doping, varying type (Fe-vacancy or O-vacancy) and number of defects. Subsequently, iron, which is known to be the best water oxidation catalyst yet very expensive, is incorporated into the hematite by co-doping, varying type (Fe-vacancy or O-vacancy) and number of defects. Under the same condition, the GNRs-ZnPpy core-shell structure had a H$_2$ production rate of 37 nmol/g, which was 15 times of the physical mixing.

**ES10.06.05**
Quantifying Strain and Dislocation Density in Assembled and Epitaxially Welded Nanocubes Harish Aarawal; Biplap K. Patra; Thomas Altantzis; Sara Bals; Annick De Backer; Sandra Van Aert and Erik Garnett; 'Center for Nanophotonics, AMOLF, Amsterdam, Netherlands; 'Electron Microscopy for Materials Research, University of Antwerp, Antwerp, Belgium.
Nanoparticles self-assembly followed by epitaxial welding has been utilized extensively to make 1D and 2D structures even with complex shapes like a honeycomb lattice. Theoretical simulations along with in-situ observation of assembly with high-resolution transmission electron microscopy (HRTEM) and small angle x-ray scattering (SAXS) has helped to shed light on the underlying mechanism of assembly and welding. Nevertheless, little is known about the strain and dislocations at the interface of the particles after epitaxy and understanding strain/dislocations at the interface is crucial for applications like photovoltaics and thermoelectrics as it can radically alter material functional properties and in turn the resulted performance. Towards this end, in this work, we examine interfacial defect and strain formation during self-assembly and epitaxial welding at room temperature of 7 nm Pd nanocubes capped with polyvinylpyrrolidone (PVP). After dropcasting the Pd nanocubes solution on a substrate (Si,N₄ grid), the PVP is removed from the surface of the nanocubes with aqueous sodium borohydride (NaBH₄) solution which was verified with X-ray photoelectron spectroscopy (XPS). During this process, the cubes move over large distances on the substrate, leading to both spontaneous self-assembly and welding to form single crystals. Subsequently, Scanning TEM, a technique that compares the positions of individual atomic columns to their position in an ideal, relaxed lattice was used to calculate the strain/dislocations at the interface of the welded cubes with different (lateral/augular) misorientations. The cubic shape characterized by its 6 chemically equivalent and atomically flat (100) faces eases welding via atomic merging and helps provide improved alignment preferentially forming single crystals leading to dislocation-free interfaces and huge reductions in strain. Even 3° angular misalignment tolerance was observed without the formation of grain boundaries.

ES10.06.06 Highly Efficient Plasmonic Membrane Activation of Peroxide for Quantized Oxidation

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Many industrial oxidation processes based on peroxide, have a difficulty of over oxidation in homogeneous solution principally due to faster oxidation rates of already oxidized species and high statistical probability of secondary oxidation near the completion of reaction. Ideal for stepwise oxidation is to limit the residence time of target molecule in a reaction zone to allow for single (or quantized) reaction events. This can be achieved in a membrane geometry where catalysis along a pore length and set flow velocity can precisely control residence time for oxidation. It is also known that Au nanoparticles can catalytically activate peroxide under light irradiation due to the formation of concentrated surface plasmon electric fields and thus hypothesized to be present in nanoporous planes. A plasmonic membrane was synthesized by evaporation of 25 thick Au films onto porous anodized aluminum oxide membranes (AAO) with pore diameters of 20-200nm. This allowed solutions of peroxide, benzene, methyl blue to flow through membrane and interact with Au surface plasmon upon exit of the membrane. Under light illumination of 10-100 mW/cm² quantum efficiencies (photon/peroxide radical) of 200-800% were seen, indicating a mechanism of field induced activation of peroxide compared to a hot electron injection mechanism. Dye and benzene to phenol oxidation are demonstrated.

ES10.06.07 Elucidating Interfacial Visible Light Absorption in TiO₂-Supported CeO₂ Nanoparticles

Photoelectrode Haiker, Kartik Venkataraman, Tu-Uyen Phan and Peter Crozier; Arizona State University, Tempe, Arizona, United States.

Generating solar fuels such as H₂ gas from water will require photocatalysts that can absorb visible light and facilitate swift charge separation/migration for surface electrochemical reactions. Photocatalysts containing “mixed metal oxide” (MMO) interfaces between TiO₂ and CeO₂, both of which are UV-absorbers on their own, have garnered attention due to their ability to drive H₂O₂ evolution from water under visible light.1,2 Visible light absorption is hypothesized to originate from partially-occupied Ce-4f states, which act as donor states within TiO₂’s bandgap, that arises from an enrichment of Ce³⁺ at the MMO interface.3 In this view, TiO₂-supported CeO₂ photocatalysts may offer a unique hierarchical geometry that confines visible-light harvesting (and charge generation) near the surface. Direct probing of the optical properties about such MMO interfaces would provide insights into the unique supported CeO₂ morphologies that produce strong, and potentially tunable, visible-light absorption.

TiO₂ supports were synthesized through a two-step hydrothermal process to yield batches of “small” (S) and “large” (L) anatase nanoparticles with average particle sizes of 15 and 66 nm, respectively, determined by powder X-ray diffraction (XRD). Subsequently, both were loaded with 6 wt% Ce via wet impregnation followed by appropriate calcination heat treatments to remove precursors. UV-visible diffuse reflectance spectroscopy shows no change in the bulk optical properties on the modified TiO₂(L) nanoparticles whereas a red-shifted bandgap from 3.2 to 2.7 eV is observed on the Ce-loaded TiO₂(S) powder which is accompanied by a white-to-yellow color change in the as-loaded powder. To compare the hydrogen evolution rates (HERs), both powders were photodeposited with 0.5 wt% Pt under visible light (∼400 nm) for one hour followed by UV-visible illumination to measure evolved H₂ gas. The HER of 6 wt% Ce/TiO₂(S) is >2x higher than that of 6 wt% Ce/TiO₂(L) owing to its increased visible-light absorption.

Aberration-corrected annular dark field scanning transmission electron microscopy (ADF-STEM) was utilized to image the two powders at atomic resolution, revealing unique CeO₂ morphologies dominating each support. On TiO₂(L), larger CeO₂ nanoparticles (e.g., ~10 nm) are ubiquitous. In contrast, TiO₂(S) is decorated by Ce single atoms and smaller CeO₂ nanoparticles. Thus, TiO₂(S) appears to contain more MMO interfaces which is consistent with its significant visible-light absorption.

Monochromated electron energy-loss spectroscopy (EELS), in the STEM, was then applied to 6 wt% Ce/TiO₂(S) to obtain valence EELS spectra from regions containing MMO interfaces. The valence EELS spectra from all regions shows the characteristic bandgap onset for TiO₂ at ~3.5 eV. However, when the probe is placed near areas containing TiO₂(CeO₂) interfaces, a broad peak centered at ~1.5 eV (with almost half of the intensity as the bulk TiO₂ bandgap signal) emerges. The relative intensity of this peak decreases in thicker regions and disappears in areas where no CeO₂⁺ species are present. This preliminary evidence suggests the presence of “interfacial” bandgap state(s) that facilitate absorption of visible light as low as 1.5 eV, which is not apparent from bulk optical spectroscopy. Future work will extend the valence EELS analysis to more regions of the sample and attempt to correlate the nanoscale optical properties with local Ce³⁺ concentration and MMO morphology (e.g., single atom vs. nanoparticles).


ES10.06.09 Interface Reconstruction Suppression Using PEALD Group-III Nitrides for Quantum Dots Solar Cells

Xinhua Zheng, Huiyan Wei, Peng Qiu, Mingzeng Peng, Sanjie Liu, Yingfeng He, Yirong Song, Yanlai An and Meiling Li; Department of Applied Physics, University of Science and Technology Beijing, Beijing, China.

Quantum dots sensitized solar cells (QDSCs) show significant potential applications due to its excellent properties including high absorption coefficient, tunable band gap and multiple excitation generation (MEG). Theoretically, the power conversion efficiency (PCE) of QDSCs can reach 44%, breaking through traditional Shockley-Queisser limit. The existence of charge recombination in the interface, however, seriously hinders further improvement of QDSCs. Use of oxides (i.e. Al₂O₃, ZrO₂, SiO₂) and/or sulfides (i.e. ZnS) as a transition layer of interface recombination is the most common method to reduce charge recombination. To the best of our knowledge, there are no reports about the application of nitrides (AIN, GaN, InN) in QDSCs. The key factor is the growth temperature of nitrides using metalorganic chemical vapor deposition or molecular beam epitaxy is extremely high, which leads to the desorption of supported quantum dots (QDs). In this study, we successfully fabricate GaN and AlN onto the QDs at a very low temperature by plasma enhanced atomic layer deposition (PEALD). The existence of nitrides can reduce recombination loss in the interface. An enhancement of open-circuit (Voc) from 0.58 V to 0.64 V is achieved for an insertion of AlN between the QDs and electrodes, while short-circuit current density (Jsc) is significantly increased up to 20% when an alternative ultrathin GaN is introduced. This results in improved efficiency of device performance are discussed in this paper. The results could open up a new way in designing and fabricating the QDSCs.

ES10.06.10 Microstructural Effects on Photocatalytic Performance in Bi₅Mo₇O₂₃AgsPO₄, Z-Scheme Systems

Kaleab M. Ayalew, Jayun Moon and Xavier Morgan-Lange; University of Nevada Las Vegas, Las Vegas, Nevada, United States.

As the world population continues to grow and access to modern industry becomes increasingly common, humanity finds itself in the midst of an environmental and energy crisis. Natural resources such as clean water are becoming increasingly scarce. A recent development in the scientific community is the study of semiconducting photocatalytic nanomaterials as a potential solution. Photocatalysts are among the most promising solutions since these materials can directly convert abundant solar energy into usable energy resources via the photoelectric effect, and produce hydroxyl group radicals which can proceed to decompose pollutants or deactivate certain microbes in a given medium.
However, it is often difficult to find an individual photocatalyst that satisfies all the requirements for an exceptional photocatalyst, such as high redox ability, narrow energy bandgap, and efficient charge-separation. The artificial heterogeneous $z$-scheme photocatalytic systems made by amalgamation of two or more photocatalysts is a replica of the natural photosynthesis process that enables the materials to overcome the shortcomings of a single component photocatalyst. In a $z$-scheme, materials with high oxidation potential, as determined by their conduction and valence band position, are paired with those that have a higher reduction potential, $\text{Ag}_2\text{PO}_4$, and $\text{Bi}_2\text{MoO}_6$. In this instance, thus creating a channel for photo-induced electron-hole pairs to recombine sacrificially. This arrangement creates the $z$-shaped path of the charge carriers and ensures the availability of electrons at the conduction band with the highest reduction potential and holes at the valence band with the highest oxidation potential. This mechanism enables composites to maintain better charge-separation and redox ability simultaneously.

Surface morphology, interface, and composition between component photocatalysts play a significant role in efficient light absorption and charge separation. Numerous strategies including morphology control have been developed recently to enhance the photocatalytic performance by maximizing the amount of light energy capture. Considering $\text{Bi}_2\text{MoO}_6$ and $\text{Ag}_2\text{PO}_4$ can absorb a broad visible light spectrum from the sun due to their relatively low bandgap energy, which makes them suitable for morphology manipulation. In this study, the correlation between the photocatalytic performance of $\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{PO}_4$ and their varied morphology and chemical characteristics is investigated. The $\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{PO}_4$ $z$-scheme is of particular interest for its exceptional photocatalytic performance, as reported by previous investigators. Therefore the purpose of this study is to design, synthesize, and test the best configuration of $\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{PO}_4$ and further improve upon an already impressive performance.

$\text{Bi}_2\text{MoO}_6/\text{Ag}_2\text{PO}_4$ $z$-scheme composite was synthesized within a facile in-situ chemical method. The crystallinity, morphology, microstructure, and light absorption wavelength range are characterized using, x-ray diffraction (XRD), field emission electron microscopy (FESEM), transfer electron microscopy (TEM), energy dispersive spectrometer (EDS) and UV–visible diffuse reflectance spectroscopy (DRS). Finally, photocatalytic performance is evaluated and reported by degrading Methylene Blue (MB) under a solar simulator with UV and visible wavelengths.

**ES10.06.11 Biomimetic Erythrocyte-Like Nanostructure for Selective Oxygen Transport**

**Grace Jiang and Lyna Zhang; Angstrom Thin Film Technologies LLC, Albuquerque, New Mexico, United States.**

H2 and O2 generation via photocatalytic water splitting process is an emerging technique in energy conversion. Selectively oxygen permeable membrane with high flux and selectivity is important for this application. In this work, we report a biomimetic ultra-thin membrane for Oxygen separation fabricated by molecular self-assembly and atomic layer deposition (ALD). ALD is a layer-by-layer deposition method that builds up a thin film with atomic precision in structure and compositions. Here we introduce the membrane fabrication by using a “plasma-defined” ALD process where the location of ALD modification is confined by plasma irradiation. Using this approach, sub-micron membrane with precisely engineered naoporous structure was fabricated. Followed by a chemical solution process, erythrocyte-like structure was achieved, leading to a highly oxygen selective membrane for oxygen purifications.

**ES10.06.12 Spray Deposition of Insulating Layers at the Rear Side of Silicon Solar Cells to Enhance their Internal Reflectance**

**George M. Spruill; Mechanical Engineering, Alabama A&M University, Memphis, Tennessee, United States.**

The solar industry has recently transitioned to manufacturing passivated emitter rear contact (PERC) cells, which are also more efficient than Al back-surface field (BSF) cells because they provide rear-side surface passivation. The goal of this experiment was to enhance the short-circuit current of PERC solar cells by inserting a low-refractive index dielectric layer between the rear passivation layer and screen-printed aluminum paste, which parasitically absorbs near-infrared light, stealing current from the cell. We used a low-cost deposition method, based on an open-air sprayer, to deposit these coatings from solution. We coated the front side of textured silicon wafers with silicon nitride (SiNx), which is used for commercial cells, and then deposited aluminum oxide (Al2O3) onto the back of some these wafers to test against reference cells with standard atomic layer deposited (ALD) Al2O3. We then deposited silicon dioxide (SiO2) on top of the sprayed Al2O3 to test if the lower refractive index of SiO2 would enhance the reflectance of our spray deposited cells. The experiment showed that samples with 10 nm ALD Al2O3 were optically equivalent to samples with 84 nm spray deposited Al2O3, and by depositing SiO2 on top of Al2O3 we were able to get a higher reflectance at longer wavelengths than with Al2O3 alone.

**ES10.06.13 Highly Efficient MIL-100(Fe)/TiO2 Composite Photocatalysts for Environmental Remediation**

**Xiang He and Wei-Ning Wang; Virginia Commonwealth University, Richmond, Virginia, United States.**

Semiconductors, such as TiO2, BiVO4, and C60, are the most widely used photocatalysts for environmental remediation due to their outstanding photocatalytic ability and low cost. However, semiconductor-based photocatalysts have two major inherent drawbacks: limited light absorption and fast electron/hole recombination. The most widely used method to solve the issues is to create semiconductor heterojunctions, with which not only the light absorption can be expanded but also the electron/hole separation can be efficiently promoted. As reported in this study, the $\text{MIL-100(Fe)}$ on $\text{TiO2}$ surface, the composite photocatalysts exhibited enhanced photocatalytic efficiency towards both tetracycline degradation and Cr(VI) reduction. The enhanced photocatalytic performance was attributable to promoted charge separation, which arose from the unique structure at the interface between $\text{MIL-100(Fe)}$ and TiO2. More specifically, during the in-situ growth of MIL-100(Fe), defect energy levels were created in the electronic structure of the composite photocatalyst, as demonstrated with the density functional theory (DFT) simulation. The defect energy levels served as sinks to capture excited charge carriers and thus retarded the recombination process, which eventually led to increased charge carrier density and enhanced photocatalytic efficiency. This work not only presents the rationally designed MOF/semiconductor composite structures for environmental remediation, but also provides mechanistic insights into the photocatalytic pathways.

**ES10.06.14 Wet Etching Mechanism of Epitaxial Er2O3 on Si for Integration to Semiconductor Technology**

**Tomas Grimova1, Tomas Dronga1 and Rytis Dargis2; 1 Institute of Photonics and Nanotechnology, Vilnius University, Vilnius, Lithuania; 2 IQE, Inc., Greensboro, North Carolina, United States.**

The rare earth oxide Er2O3 is of its exceptional and diverse properties, which can benefit in the various fields of semiconductor technology. In particular, erbium oxide is characterized by a high dielectric constant (14) and a wide bandgap (5.6 eV). It is distinguished as a high thermal resistant and chemical stable compound. Erbium oxide grown on silicon substrates reacts poorly with Si and retains its properties unchanged up to 900°C, which makes it one of the most stable compound compared to other rare earth metal oxides. Additionally, erbium oxide is noted for its high conduction band offset relative to silicon. All of these mentioned above properties are favorable for an application as a high-k gate dielectric in complementary-metal-oxide-semiconductor (CMOS) technology. Due to its stability erbium oxide can serve as a buffer layer for III-group nitrides such as GaN, InGaN, InN epitaxial growth on silicon. Furthermore, because of a large difference in refractive index between Si(n=3.5) and Er2O3(n=1.8) the stacks of Si/Er2O3 can serve as distributed Bragg reflectors for the optoelectronic devices.

The unique properties and a wide range of applications leads to necessity to investigate the patterning of erbium oxide. The easiest way to perform patterning is through the wet chemical etching. Till now, the comprehensive research have not yet been proceeded on patterning of erbium oxide. Therefore, we report on the wet etching mechanism of erbium oxide in sulphuric acid solution. After detailed analysis of wet etching kinetics, the parameters were optimized to achieve well defined structures. The etching experiments were performed on 300 nm thick Er2O3 thin films prepared on Si substrate by molecular beam epitaxy (MBE). The surface morphology studies revealed that etching mechanism was different for Er2O3(111) on Si(111) compared to Er2O3(110) on Si(100) orientation samples. Finally, GaN epitaxial growth results by metal organic chemical vapour deposition
Highly Dispersed Doped Semiconducting Nanocrystal for Efficient Opto-Electronics Application  

Talinya Gunawansa, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, Portsmouth, Virginia, United States.

Due to their unique opto-electronic properties, luminescent quantum dots (QDs) have been enhancing renewable energy efficient devices, i.e. solar cells. Although quantum dot-based organic solar cells exhibit lower efficiencies, their advantages of being lightweight, cost effective, variable materials processing, and easily tunable optical energy gaps, make them an appealing alternative to inorganic solar cells. In order to enhance the opto-electrical properties, we doped rare earth and novel metals into the semiconductors nanocrystals. Cadmium telluride (CdTe) QDs is a direct band gap materials with band gap energy of 1.52 eV and emits electromagnetic radiation in the visible region by tuning the quantum confinement of charge carriers. One pot microwave irradiation technique is an efficient, highly favored, quicker and more cost-effective synthesis route of core type CdTe nanocrystals. Cadmium telluride (CdTe) QDs is a direct band gap materials with band gap energy of 1.52 eV and emits electromagnetic radiation in the visible region by tuning the quantum confinement of charge carriers. One pot microwave irradiation technique is an efficient, highly favored, quicker and more cost-effective synthesis route of core type CdTe nanocrystals. The electromagnetic wave absorption properties of the FeNi/rGO nanocomposites exhibit enhanced properties and wide absorption bandwidth with compared with that of FeNi alloys. The minimum reflection loss of FeNi/rGO nanocomposites with a thickness of 3.0 mm can reach ~39.86 dB at 11.12 GHz, and the absorption bandwidth is up to 4 GHz. It is believed that the FeNi/rGO nanocomposites can be a best candidate for efficient electromagnetic wave-absorbing materials and widely used in practice.

ES10.06.16  
Modeling Current-Potential Responses of Homogeneous-Heterogeneous Photocatalysts  
Brian L. Wadsworth, Anna M. Beiler, Diana Khusnutdinova and Gary F. Moore; School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States.

Chemical modification of semiconductor surfaces with metal electrocatalysts provides a strategy for developing homogeneous-heterogeneous materials capable of converting sunlight to fuels and other value-added products, but their development is hampered by an incomplete understanding of the factors limiting their performance. Although SEM has been separately developed to describe photoelectrochemical or homogeneous electrocatalytic reactions, related modeling for molecular-modified hybrid photocathodes has not been as extensively elaborated. This presentation addresses the interplay between light absorption, charge transfer, and catalytic activity during photoelectrosynthetic transformations at a molecular-modified semiconductor. The analysis provides opportunities to better understand the principles governing these hierarchical constructs and develop improved photocatalytic assemblies.

ES10.06.17  
The Distinctly Enhanced Electromagnetic Wave Absorption Properties of FeNi/rGO Nanocomposites Compared with Pure FeNi Alloys  
Dong An; North University of China, Taiyuan, China.

FeNi/rGO nanocomposites were successfully synthesized by a facile one-pot method and demonstrated via powder X-ray diffraction, Raman spectra, X-ray photoelectron spectroscopy, and the scanning electron microscope. The electromagnetic wave absorption properties of the FeNi/rGO nanocomposites exhibit enhanced properties and wide absorption bandwidth with compared with that of FeNi alloys. The minimum reflection loss of FeNi/rGO nanocomposites with a thickness of 3.0 mm can reach ~39.86 dB at 11.12 GHz, and the absorption bandwidth is up to 4 GHz. It is believed that the FeNi/rGO nanocomposites can be a best candidate for efficient electromagnetic wave-absorbing materials and widely used in practice.

ES10.06.18  
Density Functional Theory Calculations of Nanopyramidal ZnO—Crystal Growth and Improved Performance in Water Splitting  
Seong Ho Park and Dong Hyun Lee; Dankook University, Gyeonggi-do, Korea (the Republic of).

In this study, we introduce a simple and effective method to induce directed self-assembly (DSA) of symmetric block copolymers (BCPs) on large area using soft grating patterns. By physically rubbing poly(tetrafluoro ethylene) (PTFE) at various temperatures near its melting point, the horizontally aligned PTFE grating patterns with ~20nm in amplitude and ~200nm in pitch distance are produced on flat Si substrates due to its low friction coefficient and high wear rate. Then thin films of symmetric polystyrene-block-poly(methyl methacrylate) copolymers (PS-b-PMMA) form on the patterned substrates as spin-coated at 2000 rpm. To induce BCP self-assembly on the patterned surface, the thin films are solvent-annealed in vapor of organic solvents like acetone, tetrahydrofuran, toluene. Even though initial morphology of the as-spun BCP thin films is irregular, the parallel orientation of lamellar nanostuctures of PS-b-PMMA is generated after solvent-annealing process. Interestingly, it is observed that those lamellar nanostructures are aligned along the pitch of underlying PTFE grating patterns and their ordering behavior are surprisingly improved by the grating patterns as compared to the BCP morphology on flat substrates. As the BCP patterns are used as templates for metal (Au, Ag, Pt) deposition process, extremely aligned metal nano-wires can be produced on the Si substrates. The ordering behavior of BCP thin films on the patterned surface is characterized by using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

ES10.06.19  
Impact of Average, Local and Electronic Structure on Visible Light Photocatalysis in Novel B4REW05 (RE = Eu & Tb) Nanomaterials  
Pradeep P. Shabangu1, 2, Rajamani Raghunathan1, Mikhail Feygenson1, Joerg Neugebauer1 and Nalini G. Sundaram; 1Poornaprajna Institute of Scientific Research, Bengaluru, India; 2Manipal Academy of Higher Education, Manipal, India; *UGC-DAE Consortium for Scientific Research, Indore, India; †Forschungszentrum Jülich, Jülich, Germany; ‡Chemical and Engineering Materials Division, Oak Ridge National Laboratory, Oak Ridge, Oak Ridge, Tennessee, United States.

B1W5O19, the simplest member of Aurivillius phase (n = 1) crystallizes in orthorhombic phase (P21a)[1]. It is found to be a potential material for visible light photocatalysis since it is a wide band gap semiconductor (Eg = 2.8 eV) with a visible light harvesting capacity at around 440 nm, and its valence band is largely dispersed due to the hybridization of O 2p and Bi 6s orbitals and conduction band is composed of W 5d orbitals[2]. To improve the light absorption capacity to the broader spectrum of visible light for efficient photoexcitation, kinetic models have been separately developed to describe photoelectrochemical or homogeneous electrocatalytic reactions, related modeling for molecular-modified hybrid photocathodes has not been as extensively elaborated. This presentation addresses the interplay between light absorption, charge transfer, and catalytic activity during photoelectrosynthetic transformations at a molecular-modified semiconductor. The analysis provides opportunities to better understand the principles governing these hierarchical constructs and develop improved photocatalytic assemblies.
photocatalysis, chemical modification of Bi$_2$WO$_6$ using transition or rare earth and p-block elements are employed[3]. It is known that doping alters the band gap and electronic structure of the material. Particularly, rare earth (RE) ions with 4f electronic configuration can absorb light from UV, Visible and IR which are associated with the f-f transitions[4], thus possibility of tuning material for wide spectrum responsive photocatalyst. In this context we have synthesized the nanostructured Rare earth (Eu & Tb) substituted Bi$_2$WO$_6$ nanoparticles by facile hydrothermal method; material crystallized in isorstruclural to monoclinic (A2/m) phase of Bi$_2$WO$_6$ having predominantly rod type morphology. Combined Rietveld refinement of synchrotron and neutron data using ordered and disordered strustures the average structure yields similar fit leading to the uncertainty in choosing the model. Further model validation is carried out through local structure probing using high Q neutron data in the short and medium range r concludes that ordered model is suitable for these nanomaterials. Rare earth substituted materials are found to be photocatalytically active for Congo-red dye degradation under visible light irradiation, the parent orthorhombic Bi$_2$WO$_6$ remained photocatalytically inactive. The increased photocatalytic activity of BiTbWO$_6$ over BiEuWO$_6$ is attributed to the enhanced charge separation as evidenced by photoelectrochemical and time resolved fluorescence study and higher mobility of excited electrons due to the nearly linear W-O-W bond angle compared to the latter. In addition our DFT calculations show that a combination of enhanced electron mobility due to large curvatures of the CB and efficient e-h separation process due to the inherent nature of electronic structure in the Tb compound is the key for improved photocatalytic activity of BiTbWO$_6$ compared to the BiEuWO$_6$ nanomaterial.

References:


Publication:
Shanbhag, P. P et al., ACS Appl. Mater. Interfaces, 2018, 10 (42), pp 35876-35887

ESI10.06.21 Noncovalent Self-Assembly and Formation of Active Porphyrin Nanostructures Gavin Heanne1, Charles Fan1, Ashley Bowman2, Jasmine Quianbao2, Casey Karler1 and Hongyou Fan1,2; 1Albuquerque Academy, Albuquerque, New Mexico, United States; 2The University of New Mexico, Albuquerque, New Mexico, United States; 3Sandia National Laboratories, Albuquerque, New Mexico, United States.

Porphyrins are a class of optically active biomacromolecular compounds that play critical roles in many biological processes including photosynthesis, and also serve as color pigments covering a wide range of the visible spectrum. As an effort to utilize these versatile porphyrins in advanced materials development, organized porphyrin nanostructures with photoactive properties have been obtained through a surfactant-assisted non-covalent self-assembly method through the cooperative interactions of the porphyrin building block zinc meso-tetra(4-pyridyl)porphine. Electron microscopic characterizations in combination with X-ray diffraction confirm that self-assembly of optically active porphyrin building blocks leads to formation of ordered nanostructures including nanorods, nanowires, nanocylinders, nanoctahedron. Investigations of variable parameters influencing the growth process show that the final product morphology is determined by reaction conditions including pH, reaction time, precursor concentration, and surfactant types. Optical characterizations using UV-vis spectroscopy and fluorescence imaging and spectroscopy show enhanced collective optical properties over the individual porphyrins, favorable for exciton formation and transport. With active and responsive optical properties, these porphyrin nanostructures are promising components for a wide range of practical applications including solar cells, photoelectrochemistry, and phototherapy. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525.

ESI10.06.22 Nanomaterial-Dependent Electrowetting Phenomena of Nanofluids Urvice Tohyahl1,2 and Nicholas Godman1; 1Azimuth Corporation, Beavercreek Township, Ohio, United States; 2Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States.

Electrowetting as a droplet actuation principle is used in many applications including digital microfluidics and reflective display devices.1 The manipulation of fluids on surfaces via electrowetting offers several advantages such as lower power consumption, high mobility of fluids and flexibility in the design of the substrates. Electrowetting on dielectric is very attractive due to large changes in contact angle between the liquid droplet and the substrate. Nanofluids (fluids containing nanoparticles) are of great interest due to reported enhanced wetting characteristics on surfaces2. Nanoparticles possess tunable optical, electrical and dielectric properties as well as varying chemical stability. They also cover a wide range of technological applications from infrared detectors, solar cells, displays to photoresponsive materials. We have evaluated the electrowetting properties of nanofluids comprised of visible II-VI (CdSe), III-V (InP) and near infrared IV-VI (PbS) and mid-wave infrared (Ag) semiconductor nanomaterials as well as ferroelectric nanomaterials (BaTiO$_3$). We will present our results on the influence of surface chemistry (different hydrophilic ligands on nanoparticles) and nanomaterial type on the electrowetting phenomena of aqueous droplets of nanofluids. We observed pronounced differences in the wetting behavior of nanofluids for all the nanomaterials studied. The study underscores the material-dependence of the wetting properties of nanofluids and the potential exploration of the optical properties of these materials in electrowetting-based platforms as well as optofluidics.

References
2) Langmuir 2015, 31, 5827–5835

ESI10.06.23 Application of Low-Energy Photoelectron Spectroscopies to Probe the Energetics in Organic Tin Halide Perovskites and the Influence of Interfacial Energetics on Photovoltaic Performance Alex M. Boehm and Kenneth R. Graham; University of Kentucky, Lexington, Kentucky, United States.

Hybrid organic-inorganic metal halide perovskites have generated tremendous interest as low-cost semiconductors for optoelectronic applications such as photovoltaics. The rapid success of hybrid organic-inorganic perovskites has thus far been centered around the lead-based perovskite derivatives; however, in recent years a sub-field has developed that seeks to substitute lead with a less toxic and more environmentally friendly alternative. Here, the clear front runner is tin, which has successfully been used in photovoltaics to achieve over 95% power conversion efficiency. In conjunction with the active layer properties the performance of optoelectronic devices is also dependent on the energetic alignment between adjacent layers. To select or design appropriate transporting materials for use in tin hybrid perovskites based optoelectronics the energetics of the active layer must be understood. Herein lies an issue where current literature regarding the valence and conduction band energies cannot reach consensus, and for a material as studied in our low energy ultraviolet and inverse photoelectron spectroscopy systems, which allow for us to minimize sample degradation, and apply them to the study of some the aforementioned factors that may contribute to the variation in reported energetics for formamidinium tin iodide. We find that air exposure has little effect on the measured energetics whereas the addition of tin(II) fluoride, which is used nearly universally in tin perovskite photovoltaics, can have great influence. Further, a series of fullerene derivatives with varying electron affinities were investigated to probe how the energetic alignment between the perovskite and electron transport layer influences photovoltaic performance.

ESI10.06.24 Exotic Magneto-Caloric Effect and Quadrupolar Interaction in Ho-Dy:Bi$_2$WO$_6$ Beomuki Cho1, Gwang-Hee Kim2 and Songhee Han1; 1Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (the Republic of); 2Physics, Sejong Univ., Seoul, Korea (the Republic of); 3Division of Navigation Science, Mokpo Maritime National Univ., Mokpo, Korea (the Republic of).

Recently, the coupled systems of the degree of freedom among spin, lattice, charge and orbital have been suggested as a breakthrough to improve conventional magnetoaloric
effect (CMCE) for magnetic refrigeration application [1]. We have investigated the MCE of rare earth tetraboride, RB₄ (R = Dy, Ho). These compounds show complex magnetic phase transition with highly degenerated system due to the interplay between magnetic and quadrupolar ordering. After the orbital degeneracy is lifted, the quadrupolar moments are geometrically frustrated through quadrupolar fluctuation. The network of quadrupolar moments forms the Shastry-Sutherland lattice (SSL) and the direction and angle of magnetic moments are limited from simple antiferromagnetic state by the strong spin-orbit coupling. Giant inverse MCE (IMCE) is observed at quadrupolar ordering temperature, which is strongly-coupled with the magnetic ground state. The exotic IMCE exhibits maximum values of 19.6 J/kgK, 19.0 J/kgK and 22.7 J/kgK at the critical applied magnetic fields of 5 T, 4 T, and 2.5 T for DyB₄, Dy₂HoB₄, and HoB₄, respectively. In particular, the exotic IMCE, which is enhanced under the critical field, decreases above the critical fields, due to the disappearance of quadrupolar ordering. These results offer new insight into the mechanism of exotic giant MCEs and magnetic cooling applications.


ES10.06.25

Rationally Designed Metal Heterostructures for Plasmon-Enhanced Photocatalysis

Han Zhang, Jianhua Yang and Jianfang Wang; The Chinese University of Hong Kong, Hong Kong, China.

Photocatalysis is a powerful way for tackling the increasingly severe environmental and energy concerns. Owing to their intriguing localized surface plasmon resonances, noble metal nanocrystals and nanostructures have shown a great potential for enhancing the photocatalytic efficiency and thereby have attracted rapidly growing interests recently. Au and Ag nanocrystals typically exhibit strong plasmonic resonances, while Pt and Pd nanoparticles typically function as versatile catalysts for various chemical reactions. In order to employ plasmon to enhance photocatalysis, much effort has been devoted to the synthesis of metal heterostructures by integrating plasmonic Au and/or Ag nanocrystals with catalytically active Pt and/or Pd nanoparticles. Such heterostructures usually exhibit enhanced catalytic performances in comparison with their monometallic counterparts due to a concerted action between the different components. However, many reported metal heterostructures are often in core@shell configurations, which can suppress the plasmonic and/or catalytic performances of the inner components. Moreover, plasmonic nanocrystals have been well known to possess hot spots, where light energy is strongly squeezed. A few studies have shown that catalytic nanoparticles deposited at the hot spots can optimize the plasmonic enhancement effect and at the same time minimize the use of expensive Pt and Pd. In this regard, we have recently performed systematic studies on the site-selective deposition of catalytic metals on pre-grown plasmonic metal nanocrystals and on their plasmon-enhanced photocatalysis behaviors.

We have recently develop a synthetic method for the site-selective overgrowth of catalytic metals on Au nanorods (NRs) and Au nanobipyramids (NBPs) (Angew. Chem. Int. Ed. 2013, 52, 10344 and Adv. Funct. Mater. 2017, 27, 1700016). Silica is first selectively deposited at the two ends of Au NRs or Au NBPs owing to the higher curvature, or deposited on the side surface when the ends are blocked by thiol-terminated methoxy poly(ethylene glycol). The pre-deposited silica component on the Au nanocrystals guides the subsequent selective overgrowth of a second metal on the exposed Au surface. Au NBP-end Pd and Au NBPside Pd heterostructures have been prepared for exploring the effect of the local electric field enhancement on the photocatalytic activity. Suzuki coupling reaction has been chosen as a model reaction to evaluate the photocatalytic performances of the different Au/Pd heterostructures. The results indicate that the photocatalytic activity is highly dependent on the site of the Pd nanoparticles, and that the plasmonic hot spots play an important role in hot-electron-driven plasmonic photocatalysis.

We have recently synthesized highly asymmetric Au nanocups, which possess a strong magnetic plasmon mode (Adv. Mater. 2016, 28, 6322). The electromagnetic field at the edge of the cup and in the opening region is strongly enhanced. We have therefore deposited Pt or Pd nanoparticles selectively at the opening region or inside the cavity of the Au nanocups and studied their photocatalytic performances. Taken together, our results offer a new insight into the rational design of highly anisotropic metal heterostructures out of two or more functional metals for various plasmon-enhanced applications, including photocatalysis, optics and biomedicine.

ES10.06.26

Formation of Novel HCSs/NbO:F Heterostructured Materials with Enhanced Carrier Separation Efficiency and Carrier Transfer

Fei Huang¹,², Zhen Li¹ and Aihua Yan¹; ¹Low Carbon Energy Institute, China University of Mining and Technology, Xuzhou, China; ²College of Technology, Arizona State University, Tempe, Arizona, United States.

As a kind of novel optoelectronic materials, niobium oxyfluoride (NbO:F) has recently attracted wide attention because of its stable crystalline phase, TiO₂-like electronic & band structure, excellent light-corrosion resistance and weak carrier recombination. However, due to its wide bandgap (3.12 eV) and low carrier separation efficiency, NbO:F is hard to be activated under visible-light irradiation to get high photocatalytic efficiency. Here, hollow carbon spheres (HCSs)-decorated NbO:F hierarchical nanostructures were successfully synthesized by a two-step hydrothermal method. The final products were characterized by a series of testing methods, such as XRD, FESEM, Raman, XPS, UV-vis spectroscopy, photocatalytic system, etc. The mechanism of carrier generation, separation, transfer and recombination for HCSs/NbO:F samples was investigated. Comparatively, NbO:F/HCSs nanostructures exhibited higher photodegradation efficiency and faster photodegradation rate in the solution of rhodamine B (RhB) under visible-light irradiation. 1.5 at.% HCSs/NbO:F samples could achieve final 97.9% RhB degradation in 50 min, while pure NbO:F samples only got 67.3% in the same time. UV-Vis spectra showed that HCSs not only enhanced optical absorption in the range of 400-1000 nm, but also extended the absorption edge, as well as tended to narrow the bandgap of NbO:F photocatalyst. That is, the enhanced photocatalytic performance can be attributed to higher spectrum absorption and faster carrier transfer from HCSs. The results here may inspire more engineering, new design and facile fabrication of novel photocatalysts with highly photocatalytic activity.

ES10.06.27

The Fabrication and Characterization of Co-Co₃(PO₄)₂-Core/Shell/Au Barcode Nanowires

Jun Hwan Moon, Yoo Sang Jeon, EunMin Yoo and Young Keun Kim; Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of).

In recent years, ceramic and noble metals have been utilized as photocatalysts [1]. In the case of catalyst, the size, shape and electrical state of the catalyst is important for obtaining sufficient catalytic activity. Especially, the unique phenomena caused by ceramic materials supported by noble metal have been researched [2]. In this prospect, the composite of ceramic and metal in the shape of multi-layer structure with varying length could provide new possibilities in catalyst area. Meanwhile, a view point of material, amorphous cobalt phosphate is an promising candidate by effectively promoting water degradation by sunlight [3]. Furthermore, it is well known that Co is an excellent electrical conductor and absorbs light of different wavelengths depending on their shape, size and interdistance of each other [4]. In this study, we propose a relatively facile and economical synthesis process fabricating 1D heterostructures, that is, core-shell/barcode nanowires (BNWs) of which each segment’s length, diameter and the thickness of shell can be easily tuned. First, we synthesized CoAu BNWs by pulsed electrodeposition method using anodic aluminum oxide (AAO) template. After that, AAO was removed with chromium phosphate and phosphoric acid. At the same time, BNWs with a core shell - noble metal structure were formed by selectively reacting only with Co layers. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive spectrometer (EDS), X-ray photoelectron microscopy (XPS), Inductively coupled plasma atomic emission spectroscopy (ICP-AES), Ultraviolet-visible spectroscopy (UV-vis) and vibrating-sample magnetometer (VSM) were employed to observe the shape and microstructure of core-shell/BNNWs. The length of each part of nanowires were successfully adjusted by the applied current densities, duration time, and phosphorus containing solution. As the face centered cubic (FCC) Au nanowires of subsequent layers, the transition of Co layers was observed from FCC to stable hexagonal closed packed (HCP) structures. Moreover, the Co phosphate shell was characterized as amorphous structures and if the reaction time is enough, Co layers are completely reacted by intruding phosphorus changing into a perfect ceramic-noble metal nanowire. X-ray based measurement system and ICP-AES let us understand the diffusion of phosphorus. In addition, UV-vis provides optical property of synthesized nanowires. Finally, we verified the catalytic properties depending on the dimension of each part.

References


ES10.06.28

Electronic Textiles Based on Aligned Electrospun Belt-Like Cellulose Acetate Nanofibers and Graphene Sheets—Portable, Scalable and Eco-Friendly Strain Sensor

Xu WanLin, Fu WanLin and Dai Yunqian; Southeast University, NanJing, China.

Electronic Textiles based on aligned electrospun belt-like cellulose acetate nanofibers and graphene sheets are portable, scalable and eco-friendly strain sensors. Aligned electrospun belt-like cellulose acetate nanofibers were synthesized through single-nozzle electrospinning. Graphene sheets were subsequently deposited on the nanofibers to obtain the conductive sensor. The strain sensitivity of the developed sensors is around 260 Ω% for a strain range of 10%. The fabricated sensors were used to detect the strain of a human finger. The results show that the developed sensors provide a high sensitivity and good reversibility. The fabrication process is simple and scalable and can be extended to the production of other flexible electronic devices.
Recently there is strong interest in flexible, and wearable electronics to meet the technological demands of modern society. Environmental-friendly and scalable electronic textile is a key area that is still significantly underdeveloped. Here, we describe a novel strain sensor composed of aligned cellulose acetate (CA) nanofibers with belt-like morphology and reduced graphene oxide (RGO) layer. The unique spatial alignment, microstructure and wettability of CA nanofibrous membrane facilitate their close contact with deposited GO colloids. After a portable and fast hot-press process within 700 s at 150 °C, the GO on CA membrane can be facile reduced to conductive RGO layer. Moreover, the connection among contiguous CA nanofibers and the interaction between GO and CA substrate were both highly enhanced, and thus a superior mechanical strength with Young’s modulus of 1.3 GPa and small sheet resistance lower than 10 KΩ. Therefore, the conductive RGO/CA membrane was successfully utilized as a strain sensor in a broad deformation range and versatile deformation types. Moreover, the distinctive mechanical strength under different stretch angles endowed the well-aligned RGO/CA film with intriguing sensitivity against stress direction. Such a cost-effective and environmentally-friendly method can be easily extended to scalable production of graphene based flexible electronic textiles.

ES10.06.29
Nanomaterials for Mesoscopic Perovskite Solar Cells Zheqin Zhang; Guilin University of Electronic Technology, Guilin, China.

To meet requirements of low cost, fully printable mesoscopic perovskite solar cells (MPSCs) based on carbon counter electrode are investigated. Devices with excellent long-term stability and a certified PCE of 12.8% are successfully fabricated by mixing MAPbI3 with an additive of 5-ammoniumvaleric acid iodide (5-AVAI). In the presentation, a simple and effective way is developed for enhancing the performance and long-term stability of hole-transporting MPSCs, by incorporating an additive of iodide benzylamine (BAI) into the methyl ammonium iodide. BA-MAPbI3 based fully printable MPSCs achieves a PCE of 12.69%, in comparison with 6.43% of the controlled MPSCs. The introduction of BAI induces better pore filling in the perovskite TI2O3 scaffold, reduces defect concentration in perovskite films, and induces better contact with TI2O3 scaffold. All the factors result longer excitation lifetime and higher quantum efficiency in BA-MAPbI3 MPSCs. Furthermore, BA-MAPbI3 MPSCs show excellent stability, the devices could keep 80% of origin power conversion efficiency for over 500 hours in ambient air under continuous light.

Acknowledgement: This research was financially supported by the National Natural Science Foundation of China (61564003, 61774050), and the Guangxi Natural Science Foundation (2015GXNSFGA139002), and the Guangxi Bagui Scholar program.

References (12 pt)
5. C. Xu, Y. Hu,* Z. Zhang, Y. Sheng, P. Jiang, H. Han, J. Zhang*, submitted.

ES10.06.30
Spray Deposited ZnO/Bi2O3 Thin-Film Heterojunctions with Enhanced Visible Photocatalytic Activity Juliette Reyes Arrango and Monserrat Bizarro; Instituto de Investigaciones en Materiales, UNAM, Mexico, Mexico.

The wide interest of finding new photocatalysts that can efficiently use the solar energy as activating source has led to the development of different strategies. The most common one is the introduction of dopants into a semiconductor’s matrix, in order to decrease its bandgap. However, the bandgap diminution entails also a decrease in the oxidation and reduction power of the photocatalyst, reducing its final efficiency. By contrast, the coupling of two different semiconductors seems to be a better alternative, as the best characteristics of each other can be exploited. In this work, we developed heterostructures based on the coupling of two semiconductors, zinc oxide (ZnO) and bismuth oxide (Bi2O3), using the pneumatic spray pyrolysis technique. The ZnO/Bi2O3 heterostructures were obtained on glass substrates with the help of aluminum masks with different configurations. The configuration of the masks was optimized based on the exposed area of each semiconductor, in order to maximize their coupling. The structural, morphological, optical and electronic properties of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis diffuse reflectance spectroscopy and photoluminescence (PL). Finally, the photocatalytic activity for the degradation of indigo carmine (IC) dye was evaluated under visible light using UV-Vis spectrophotometry technique. ZnO films present a nano-flake morphology with nano spikes that provide high surface area, while Bi2O3 coatings appear as dense clusters or agglomerates. The results show that the heterostructures are effectively activated under visible light showing an enhanced photocatalytic response compared to the independent ZnO and Bi2O3 films. This synergistic effect is achieved due to the visible light excitation of the Bi2O3 film and the subsequent charge transfer to the ZnO film.

ES10.06.31
Highly Transparent Catalysts for Solar Fuels Applications via Mesoscale Photonic Design Wen-Hui Cheng, Matthias H. Richter, Sisir Yalamanchili, Phillip Jahelka, Pin Chieh Wu and Harry Atwater; California Institute of Technology, Pasadena, California, United States.

Direct solar-to-fuel generation using a photocathode-based photoelectrochemical cell requires a light absorber which can provide the photovoltage necessary to overcome the thermodynamic potential (1.23V for H2/O2, 1.33V for CO2/O2) as well as the catalyst overpotentials for both cathode and anode reactions. To realize high solar-to-fuel efficiency, it is necessary to maintain a catalytic current density close to the light limiting photocurrent density for a solar-driven light absorber, which can be fulfilled when catalyst ensembles are highly transparent. Recently, we reported a record solar-to-hydrogen efficiency using a tandem III-V semiconductor photoelectrode based solar photoelectrochemical cell with an optically transparent catalyst comprised of a dense array of Rh metal nanoparticles1. For CO2 reduction, a different approach is required, given the opaque nature and limited activity of most CO2R catalysts. Here, we report and demonstrate two light trapping photoredox strategies to create highly active and effectively transparent catalyst structures for photocathodic CO2 reduction: i) an effectively transparent catalyst consisting of arrays of micron-scale triangular cross-sectional silver grid fingers, which is capable of redirecting the incoming light to the open areas of the PEC cell without shadow loss, and ii) arrays of mesophotonic dielectric cone structures that are made as tapered waveguide light coupler to efficiently guide incident light through apertures in an opaque catalyst into the light absorber. To validate these designs, numerical calculations using full wave electromagnetic simulations were used to investigate the optical response. We find that a mesoscale silver grid array with triangular cross-section lines and metal coverage of ~ 50% exhibits negligible additional reflection loss. For the nanostructure dielectric cone light couplers, <10% reflection (>90% transmission) is achieved experimentally for metal (Cu) coverage as high as 70%. Both catalyst designs will be described in detail, including simulations and fabrication methods, as a guide to efficient catalyst design for photoelectrochemical solar fuels generation.

Reference

ES10.06.32
Secondary Emissive Coatings from ALD—Metal Oxides and Fluorides Maximilian Gebhard1, Mark Popecki2, Till Cremer1, Michael Minot1, Anil Mane1 and Jeffrey Elam1; 1Argonne National Laboratory, Lemont, Illinois, United States; 2R&D, Incom Inc., Charlton, Massachusetts, United States.

An important building block for detector devices are signal amplifiers, such as microchannel plates (MCPs). Due to the electron cascade produced within the high voltage-biased MCP pores, incident electrons, photons, or ions can be amplified by 10^6, making MCPs highly efficient in photon-counting devices. Moreover, since the MCP comprises millions of parallel pores, these devices are ideal for imaging applications astronomy, high-energy physics, medicine, etc. Recently, MCPs have been fabricated by functionalizing capillary array glass using atomic layer deposition (ALD) coatings to impart the necessary electrical resistance and secondary electron emissive (SEE) properties. Considering the complex geometry of the MCPs, ALD is ideal for depositing these functional coatings with high precision and conformity. Thus far, a limited number of ALD materials (i.e. Al2O3 and MgO) have been evaluated as SEE layers in MCPs. While these materials show great performance in real-life MCP applications, chemical reactions between these SEE materials and the underlying resistive coatings are a possible limitation to their ultimate performance. In addition, the reaction of MgO SEE layers with ambient H2O and CO2 changes the surface chemistry and causes a drop in the SEE value. These issues motivate the study of alternative ALD materials to function as SEE layers in MCPs.

We present here the development and evaluation of ALD metal fluoride and mixed metal oxy-fluoride coatings as potential SEE layers in MCPs. We also investigated the
influence of H$_2$O and CO$_2$ exposure on the SEE surfaces to understand the effect of these ambient compounds on the properties of the coatings. The ALD mechanism was studied using in-situ quartz-crystal microbalance (QCM), quadrupole mass-spectrometry (QMS), and Fourier transform infrared spectroscopy (FTIR) measurements. The materials were analyzed to determine their structure and composition using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray reflectivity (XRR). The ALD SEE layers were deposited on commercial MCP substrates to evaluate the electronic properties and to measure the gain and stability during operation.


**ES10.06.33**

**Novel Method of Transferring CNT Forest to Any Substrates**

Chi P. Haynh, Masa Ito and Raquel Ovalle; Nano science and nano technology, Lintec of America, Richardson, Texas, United States.

Carbon nanotubes (CNTs) have many attractive properties, and show promise in a wide variety of applications. Demonstrated is a light absorption material, EMI shielding and or sound absorption material utilizing CNT materials in the form of a vertically aligned CNT forest. The CNT forest is grown via chemical vapor deposition and requires catalyst, carbon source, inert gas and hydrogen. Hard substrates such as quartz, silicon wafer, stainless steel or aluminum are generally used as these can withstand the high temperatures required for CNT growth. Such hard substrates make it difficult to use the CNT forest in applications, particularly those requiring complex geometric configurations or flexibility.

The fragility of the CNT forests makes it a challenge to transfer them from their inflexible growth substrate onto a target substrate. In this work we report a novel method of transferring CNT forests onto an arbitrary substrate, including common polymer films such as PET. The developed technique is also able to alter the alignment angle of the CNT forest relative to the substrate: 90 degree (high angle), 45 degree (mid angle) and 25 degree (low angle). Typically, an adhesive is used to transfer the CNT forest, but in some cases the adhesive is replaced with a non-adhesive material.

**SESSION ES10.07: Solar Cell**

**Session Chairs: Weiwei He and Zhi Zheng**

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 121 A

**8:30 AM **

**ES10.07.01**

**Chromophore-Catalyst Assemblies for Solar Fuels**

Kirk Schanz; The University of Texas at San Antonio, San Antonio, Texas, United States.

The dye-sensitized photoelectrochemical cell (DSPEC) represents a novel approach to combining molecular chromophores and catalysts with semiconductors to effect light driven production of solar fuels. A multidisciplinary approach has been used to develop and study molecular and polymer assemblies for light driven water oxidation at a DSPEC photoanode and proton reduction at a photocathode. The work aims to understand mechanisms and dynamics for the photoprocesses occurring at the molecular/semiconductor interfaces. The talk will present an overview of work done during the past several years, involving the design, construction and study of molecular and polymer-based assemblies of light absorbing chromophores and catalysts, primarily aimed at water oxidation at the DSPEC anode.

**9:00 AM **

**ES10.07.02**

**An In Situ Room Temperature Route to CuBils Based Bulk-Heterojunction Perovskite-Like Solar Cells**

Zhi Zheng and Yan Lei; Xuchang University, Xuchang, China.

Both bismuth and copper are toxic and relative low-abundant elements suitable for lead-free halide perovskite-like photovoltaic devices. Here, we report a highly facile route for in-situ producing copper-bismuth-iodide (CuBiI$_3$) thin films directly on ITO substrate at room temperature, by utilizing a Bi-Cu alloy layer as precursor. X-ray diffraction and TEM results verified the formation of well crystalized CuBiI$_3$ thin films with (222) facet orientation. The transient photovoltage (TPV) analysis revealed that the CuBiI$_3$ is an n-type semiconductor with preferable photoelectric conversion character comparing with CH$_3$NH$_3$PbI$_3$ perovskite. A suitable band gap of ~1.81 eV for solar absorption and photovoltaic was illustrated by UV-Vis, PL and IPCE spectra in its experiments. It is very interesting to note that the subsequent spin-coating process of the classical Spiro-MeOTAD organic solution with TBP and acetonitrile resulted in a completely mixed, dense, and smooth CuBiI$_3$: Spiro-MeOTAD bulk-heterojunction film. The preliminarily fabricated simple sandwich structures of ITO/ CuBiI$_3$: Spiro-MeOTAD: Au hybrid solar cell devices displayed efficient photovoltaic performance with the PCE up to 1.119% of the best sample. The current room temperature direct metal surface elemental reaction (DSMER) method may provide a new insight for future all-inorganic lead free perovskite-like A$_n$B$_m$X$_p$ compounds and high performance photovoltaic devices.

**9:30 AM **

**ES10.07.03**

**Hierarchical Zinc Oxide Nanostructures for the Photochemical Reduction of Bicarbonate to Solar Fuels**

Hanging Pan and Michael Heagy; New Mexico Institute of Mining and Technology, Socorro, New Mexico, United States.

Zinc oxide (ZnO) is an earth abundant, non-toxic, and low-cost material that has been used widely for photocatalytic water splitting, gas sensing, and dye degradation. In this study, several ZnO structures were synthesized, characterized, and tested for the photocatalytic reduction of bicarbonate to formic acid, an intermediate to methanol, a high-octane-number fuel. The different ZnO morphologies studied include micron- and nano-particle ZnO, rods, wires, belts, and flowers. ZnO was also synthesized from the direct calcination of zinc acetate, which provided a cheap and large-scale synthesis method to produce ZnO. The photocatalytic efficiency of the synthesized ZnO was compared to TiO$_2$ alone. The enhancement is predicted to be due to the plasmon-induced excited charge transfer from TiO$_2$ to the conduction band of TiO$_2$: TiN. The enhancement is predicted to be due to the plasmon-induced excited charge transfer from TiN to the conduction band of TiO$_2$: TiN. The enhancement is predicted to be due to the plasmon-induced excited charge transfer from TiN to the conduction band of TiO$_2$: TiN.

**9:45 AM **

**ES10.07.04**

**Plasmon-Enhanced Photocatalytic Reaction on Titanium Nitride Nanoparticles-Combined Experimental and Theoretical Study**

Alyssa Beierle$^1$, Paul Gieri$^2$, Alejandro Manjavacas$^3$ and Sanchari Chowdhury$^4$; $^1$New Mexico Tech, Socorro, New Mexico, United States; $^2$Physics and Astronomy, The University of New Mexico, Albuquerque, New Mexico, United States.

Plasmon-enhanced photocatalytic reaction on TiO$_2$ under solar light using alternative plasmonic titanium nitride(TiN) nanoparticles is studied. The excellent chemical stability at elevated temperatures and higher integrated absorption efficiency under a solar light in comparison to conventional plasmonic nanomaterials (silver and gold) make TiN a promising candidate for this application. We observed an efficient production of formic acid through simultaneous photoreduction of bicarbonate and oxidation of glycerol in the presence of TiO$_2$/TiN composite nanocatalysts in an isothermal condition. The photocatalytic productivity of formate with TiO$_2$/TiN composite is significantly (6 times) higher than TiO$_2$ alone. The enhancement is predicted to be due to the plasmon-induced excited charge transfer from TiN to the conduction band of TiO$_2$: <div>Interestingly, under solar light TiN alone can photo catalyze the reaction more efficiently than TiO$_2$ nanocatalyst (Degussa, P-25). The enhanced performance of TiN is attributed to the efficient hot electron transfer from TiN nanoparticle core to native thin (1-2 nm) amorphous titanium oxide shell, where the reaction takes place. The characterization of TiN nanoparticles after the reaction confirmed that TiN nanoparticles could remain stable under reaction conditions for extended periods of solar light exposure (8 hours). Comprehensive theoretical analyses
including fully numerical solutions of Maxwell equations to understand the optical properties of the nanostructures are done to support the experimental observation.</div>

10:00 AM BREAK

SESSION ES10.08: Photoelectrocatalysis
Session Chairs: Weiwei He and Zhi Zheng
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 121 A

10:30 AM #ES10.08.01
Design Strategies for Novel Catalyst for (Photo)Electrocatalytic CO₂ Reduction Reaction Francesco Maria Tongi; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

( Photo)electrocatalytic reduction of carbon dioxide offers an efficient strategy to reduce the presence of greenhouse gases in the atmosphere while concurrently producing valuable carbon-based products. However, existing ( photo)electrocatalysts for this process are insufficiently active or selective for attractive energy dense products, particularly in the face of the competing hydrogen evolution reaction ( HER ). Here, we present design strategies for the synthesis of novel ( photo)electrocatalysts for CO₂ reduction. We provide different examples of catalytic systems that can reveal design principles that enable development of active and selective catalysts and provide further insights into the reaction mechanism.

References:

11:00 AM #ES10.08.02
Functionalizing Si with WO₃ or BiVO₄ for Photoelectrochemical Applications Guido Mui¹, Alexander Milbrat², Bastian Mei², Jurriaan Huskens² and Ronald Jong²; IPCS Group, MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; University of Twente, Enschede, Netherlands.

In this presentation recent efforts to create Si based photoanodes for photoelectrochemical applications will be discussed. Particular attention will be paid to WO₃ films, using an ITO interface. WO₃ on ITO/Si was found to rapidly lose performance in acidic media, which we assume to be due to the formation of adsorbed hydroperoxo species. When nanometer thin Pt was used to interface WO₃ with Si, stability and enhanced performance could be induced by deposition of TiO₂, prior to deposition of IrO₂. The effect of the height and spacing of microwires of Si on the photoelectrochemical performance of deposited BiVO₄ will also be addressed. Microwire substrates with BiVO₄ underperformed compared to BiVO₄ on flat surfaces. We predominantly attribute this to detrimental diffusion limitations of the redox species within the internal volume of the microwire arrays, in agreement with existing literature and observations regarding the electrodeposition of BiO, used as precursor for BiVO₄. Our results assist in developing high-efficiency PEC devices.

11:30 AM ES10.08.03
Solar-Driven Photocatalytic CO₂ Reduction in Water Utilizing a Ru Complex Catalyst on p-Type Fe₂O₃ with a Multiheterojunction Keita Sekizawa, Shunsuke Sato, Takeo Arai and Takeshi Morikawa; Toyota Central R&D Laboratories, Inc., Nagakute, Aichi, Japan.

To accomplish a practical CO₂ reduction system aimed at artificial photosynthesis, a hybrid system composed of a metal complex catalyst and a semiconductor photosensitizer has become a feasible approach, and the conversion efficiencies of such systems have been improving. However, there is still little research focusing on material cost and operation in water. Hematite (α-Fe₂O₃) is one of the most abundant and low-cost semiconductor materials, and can absorb a substantial amount of solar light (Bandgap: 2.1 eV). Although a usual α-Fe₂O₃ exhibit n-type conductivity, doping with ions such as Mg²⁺ and Zn²⁺, and N⁺ into α-Fe₂O₃ induce p-type conduction. We have reported that N,Zn-codoped α-Fe₂O₃ (N,Zn-Fe₂O₃) exhibited high cathodic photocurrent for O₂ reduction.[1] However, there are two issues with p-type Fe₂O₃; in that the charge separation property is inefficient and it easily corroded due to the self-reduction reaction under the reducing conditions in the CO₂ saturated aqueous electrolyte. To overcome the issues, a TiO₂ layer was introduced onto the surface of p-type N,Zn–Fe₂O₃ to passive surface defects. In addition, to ensure efficient electron transfer, a thin Cr₂O₃ layer was also inserted between N,Zn–Fe₂O₃ and a bottom side conductive oxide layer to generate a favorable band alignment for hole transfer. To optimize a metal complex – semiconductor hybrid photoelectrode, a Ru complex polymer with a low CO₂ reduction potential and an electron network with polypyrrole chains was determined to be the best combination with TiO₂/N,Zn–Fe₂O₃/Cr₂O₃.[2] We have successfully accomplished stable CO₂ reduction reaction coupled with H₂O oxidation in the absence of an external electrical bias by constructing a tandem cell reactor with an n-type SrTiO₃ photoanode.

Reference

SESSION ES10.09: Photocatalysis
Session Chairs: Dan Qu and Wenbo Wei
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 121 A

1:45 PM ES10.09.01
Consciously Constructing Z-Scheme Photocatalysis via Photo-Deposition Method for Improving Photocatalytic Activity Wenshuai Jiang and Zaicheng Sun; Beijing University of Technology, Beijing, China.

Heterojunction and direct Z-scheme nanostructures are two typical representatives of an efficient photocatalyst, which is composed of two semiconductors. However, it is a great challenge to construct each of them on purpose. Photo-deposition technique can be a potentially powerful tool to regulate the electron flow direction for constructing these nanostructures. So, can we refer to the controllability of photo-deposition on the direction of charge flow to achieve a direct Z-scheme nanojunction construction? Based on the above discussion, we synthesized Fe₃O₄/g-C₃N₄ and TiO₂/CdS composites by photocatalytic oxidation deposition and photocatalytic reduction deposition, respectively. In order to verify both systems are the Z-scheme type junction, charge-tracking experiments were performed on both of them. The charge tracking experiments of Fe₃O₄/g-C₃N₄ composites obtained by oxidative deposition of Fe₃O₄ on g-C₃N₄ substrates show that the oxidation sites of the composites are located in Fe₃O₄ which is the same as the expected results. At the same time, TiO₂/CdS composite material is obtained by using TiO₂ nanorods reduction deposition of CdS, the charge tracking results showed that the reduction site of the composite was located in CdS, which proved that direct Z-scheme was reached through photo-deposition.
Innovations in photoelectrode architecture can continuously increase surface area, enhance light absorption and improve charge transport, and thereby increase overall power conversion efficiency. In the past, nanostructures of varying complexities, from one-dimensional nanotubes, nanowires and nanorods, to two-dimensional films and nanonets, and three-dimensional (3-D) porous structures, were reported with superior performance. In this presentation, branched 3-D nanostructured materials, especially ZnO, were discussed. To elevate the spatial occupancy of one-dimensional ZnO nanostructures and explore new structures as efficient electrodes for industry-level photoelectrochemical (PEC) water splitting into usable H2 fuel, we have developed procedures to fabricate nanoforest and “caterpillar-like” ZnO nanostructured network (CZN) for PEC applications. Moreover, by fine-tuning the synthesis procedure and manipulating their growth process, the dependence of their PEC properties on geometry factors of the unique branched nanostructures was controlled. As a result, the branched ZnO array nanostructures of tunable surface-to-volume ratio and roughness have been investigated. They offer mechanically and electrically robust interconnected networks with open micrometer-scale structures and short hole diffusion length. The preferential light-material interaction and charge separation to maximize the photo-to-hydrogen conversion efficiency were further studied. When used as photoanode, our branched nanostructures not only favor sunlight harvesting with multireflection ability, but also suppress the recombination of photogenerated charge. To sum, these novel branched nanostructures represent a new generation of photoelectrodes for high-efficiency solar energy harvesting and conversion to clean chemical fuels and hold bright potential for a wide range of practical applications in renewable energy.

Size-Dependent Photoresponse of Plasmonic Aluminum Nanoparticles
Yan Cheng, Kenneth J. Smith, Ebsuka S. Arintze, Tina Gao, Arthur E. Bragg and Susanna M. Thon; Johns Hopkins University, Baltimore, Maryland, United States.

Aluminum has attracted a great deal of attention as a plasmonic material in recent years due to its high abundance and low toxicity. Compared to frequently used gold and silver, it exhibits relatively high free carrier density, and the localized surface plasmon resonances (LSPRs) of aluminum nanoparticles can be tuned from the ultraviolet to the visible wavelength regime by controlling the nanoparticle size and shape. Aluminum nanostructures have been successfully used as sensitizers in photocatalysis for absorption.
enhancement and higher photocatalytic efficiency and selectivity. Since this process relies on hot carrier injection into the semiconductor photocatalyst, investigations on carrier relaxation dynamics in aluminum nanoparticle systems are critical in order to develop optimal architectures for efficient carrier injection. In an early study, we synthesized aluminum nanoparticles with diameters of approximately 100 nm in the solution phase and characterized used high-resolution transmission electron microscopy to show that these particles contain a 3.7 nm thick self-limiting surface oxide layer. Using transient absorption spectroscopy (TAS), we demonstrated that these large nanocrystals show a decreased transmission in the visible and near infrared regions while displaying a bleach in the wavelength that corresponds to the aluminum interband transition. These large particles show fast energy transfer to the solvent, on a timescale of approximately 250 ps, which is mediated by the thin oxide shell according to an extended two interface model for thermal transport. Here, we prepare aluminum nanoparticles with tunable sizes in the range of 70 nm to 130 nm in diameter with dipolar LSPRs ranging from 350 nm to 580 nm in wavelength. TAS is employed to study the size-dependent thermal relaxation dynamics. We show that the frequency of phonon oscillation is inversely proportional to the size of the particles which is consistent with acoustic modeling results. Furthermore, we find that the energy relaxation timescale decreases with decreasing nanoparticle diameter. For all particle sizes, the oxide shell mediates a faster energy exchange process than that predicted for metal-only particles. These energy dissipation studies are crucial for designing nanostructures with optimized sizes and surface profiles that will be favorable for utilizing local temperature variations and charge transfer to enhance photocatalytic rates in heterogeneous systems.

3:45 PM ES10.09.07
Photocatalytic System with Built-In Light Supply Based on Optical Waveguide Effect
Min Du; Shandong University, Jinan, China.

Light propagation limitation in wastewater constrain the photocatalytic water treatment system in type of large-area with thin in depth. The industrial water treatment with photocatalytic technique was constrained by the land shortage. To realize the 3D photocatalytic system, the light propagation in deep water was overcome via the optical fiber based on the optical waveguide effect. One-dimensional TiO$_2$ array are synthesized on commercial optical quartz fiber by a one-step hydrothermal process. The light propagation in the optical fiber and export at the junction between optical fiber and TiO$_2$ nanorods. The light propagation in the TiO$_2$ nanorods would be absorbed in high efficiency, which results in a high rate of the light utilization. This built-in light supply mode can solve the light propagation in deep water. The demo device assembled by TiO$_2$ functioned optical fiber exhibits excellent photocatalytic performance implying its high potential in industrial application.

4:00 PM ES10.09.08
Amazing Acid-Mediated Porphyrin Self-Assembly with NIR Absorption as Highly-Efficient PTT Platform for Curing Tumors
Jinghui Wang; Key Laboratory for Special Functional Materials of the Ministry of Education, Kaifeng, China.

Exploring the synthesis of photosensitizers that not only have strong absorption in the near-infrared region but also achieve rapid temperature rise in a short period of time are required for excellent photothermal therapy. Porphyrins as a class of biological macrocyclic conjugated molecules with good biocompatibility are more and more used in biological diagnosis and treatment. However, to make ordinary porphyrin molecules achieve strong absorption in 800 nm near infrared region and enhance penetration ability in PTT is still unresolved. Here we report a proton acid doping porphyrin self-assembly method to construct strong NIR absorbance near 1000 nm photothermal conversion agents using 5,10,15,20-tetrakis (4-aminophenyl) porphyrin (TAPP) as optical active precursor. A series of morphologies including nanosheets (NSs) and nanorods (NRs) as amorphous nanoparticles (NPs) are synthesized with controlled size and dimension. The morphology and absorption spectra can be regulated by adjusting the types of surfactant micelles and the addition amount of protonic acid though adjusting the weak interaction forces between the assembled molecules. Owing to the inner core protonated of the TAPP in NPs effectively improved NIR-absorption and complete quenching of fluorescence. Ultimately obtaining a morphologically dependent NPs capable of efficiently utilizing NIR light energy to thermal energy conversion is obtained. The NPs connected with ERGD have been used in the treatment of tumor-bearing mouse models to achieve excellent therapeutic effects. This method of adjusting the spectral changes by adjusting the weak interaction between the assembly elements has a good extension value.

4:15 PM ES10.09.09
Controllable Self-Assembly of Porphyrin with Photocatalytic Water Splitting Under Visible Light
Ronghui Cao; Key Laboratory for Special Functional Materials of the Ministry of Education, Henan University, Kaifeng, China.

Photocatalytic hydrogen production from water splitting is considered as one of the promising ways to provide clean fuels that can convert solar energy into chemical energy. In the past years, researchers have made great efforts to develop various inorganic and organic materials systems as photocatalysts for water splitting. Photocatalytic water splitting includes three steps: (i) photocatalyst absorbs light; (ii) photogenerated charge separation; (iii) surface chemical reaction. Only by enhancing the efficiency of each step can the efficiency of photocatalytic water splitting be improved. Directional separation of photogenerated charge is more studied in inorganic semiconductor photocatalysis, but little research has been done on organic photocatalysis. Here, we reported an emulsifier-assisted co-solvent method to fabricate porphyrin nanomaterials using Pd meso-tetra-(4-carboxylphenyl) porphyrin as building blocks. The specific arrangement of aggregates were spontaneously constructed driven by confined noncovalent interactions of hydrogen bonds, π-π stacking, hydrophilic-hydrophobic. The four carboxyl groups and center metal Pd within the PdTCPP molecular endowed strong hydrogen bonding and axial coordination between porphyrin and emulsifier. These assemblies had a wide absorption spectrum at 400-700 nm, which was good for absorbing visible light. These assemblies were used for photocatalytic hydrogen production under visible light and the result exhibited the outstanding hydrogen evolution rate of 9.38 mmol/g/h in the absence of Pt particles as cocatalyst in our work. The rate of photohydrogen production increases to 138.94 mmol/g/h after photocatalytic deposition of Pt nanoparticles. What's interesting is that the Pd nanoparticles are mainly on the edge of the assemblies. This indicated that the edge of the assemblies was the electron transport channel. The hole transport channel remained to be studied.
Currently over 95% of hydrogen is made from fossil fuels through natural gas reforming or coal gasification. A major part of reducing carbon emissions must therefore include sources of renewable hydrogen. In addition, capture of existing carbon dioxide sources and subsequent conversion to higher value chemicals also requires a hydrogen source. Using hydrogen from traditional sources for this purpose does not make environmental sense, since the net effect is just shifting where the carbon dioxide is emitted geographically. Large scale, cost competitive sources of renewable hydrogen are critical in moving to more sustainable processes worldwide.

Low temperature electrolysis has decreased significantly in cost while increasing in scale over the last several years, and there continue to be large opportunities for additional cost reduction and performance improvements. With the advent of low cost renewable electricity, particularly in times of excess capacity when storage is most needed, electrolysis is reaching the production and cost scale to provide a viable solution. However, as research activities have increased, differences in testing conditions, reporting comparisons, cell designs, and other factors convolute data interpretation and can lead to misleading conclusions. In addition, insufficiently controlled procedures can mask effects. This talk will describe some of the complex interactions that need to be considered, and current efforts in developing community-wide tests ranging from ex-situ material screening protocols to realistic device testing. This work is part of an ongoing program across all of the major advanced water splitting technologies, the subject of this symposium and the parallel high temperature water splitting symposium.

10:45 AM ES11.01.02/ES12.01.02
**Development of Protocols and Standards for Photoelectrochemical Water-Splitting**  
Chengxiang Xiang; California Institute of Technology, Pasadena, California, United States.

Cost competitive hydrogen generation at scale using sunlight and water can play a significant role in decarbonization of our society. In recent years, photoelectrochemical (PEC) water splitting has made significant progress in materials discovery, mechanistic understanding, as well as in achieving un-precedent solar to hydrogen conversion efficiencies in the laboratory scale. To further advance this technology and reach the bench scale (0.1 kg/day) and sub-scale (2 kg/day) operational platforms, development of standard protocols and best practices for benchmarking materials and devices as a community is critical. Standardized methodologies and best practices also provide significant benefit in accelerated RD&D of advanced materials and cross-cutting efforts.

In this presentation, I will talk about recent community-based efforts in defining targets, best practices and gaps in PEC hydrogen production in HydroGEN Energy Material Network (EMN) consortium. Specific challenges related to PEC will be discussed including scale up challenges, integration challenges at the component level, lack of performance data and test protocols for photoelectrodes under real-world operating conditions and lack of fundamental understanding of photoelectrode corrosion mechanisms and accelerated test protocols. In addition, I will also present a brief summary and status reports on lab EMN nodes/capabilities for PEC water-splitting. Key takeaways from a recent HydroGEN Benchmarking&Protocols Workshop and DOE PEC Working Group Meeting will also be discussed.

11:00 AM ES11.01.03/ES12.01.03
**Framework and Test Protocols for High Temperature Electrolysis**  
Olga Marina; Pacific Northwest National Laboratory, Richland, Washington, United States.

Hydrogen production via water electrolysis is considered to be an efficient way to smoothen the fluctuating power output of renewable energy sources and avoid oversupplies. This presentation will provide the status of the standards and protocols development for high temperature electrolysis (HTE) technology within the US DOE HydroGEN Energy Materials Network Consortium. The current material standards, advanced characterization techniques, best practices and testing protocols from screening of fundamental material properties to device level benchmarking will be discussed to address key challenges and leverage technical advancements across the different water splitting technologies.

11:15 AM ES11.01.04/ES12.01.04
**Framework and Test Protocols for Solar Thermochemical Water Splitting**  
Ellen B. Stechel; LightWorks and School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States.

This presentation will provide the status of standards and protocol development within the US DOE HydroGEN Energy Materials Network (EMN) Consortium for advanced water splitting using concentrated solar thermochemical redox cycles, generally referred to as STCH, solar thermochemical hydrogen. Cost competitive water splitting to produce hydrogen at scale using concentrated sunlight can contribute significantly to a net CO₂ neutral society. In recent years, STCH has made significant progress. Working as a community will further advance STCH technology with a goal of reaching demonstration scales of multiple kilowatts with promising redox active materials. The development of standard protocols, definitions, metrics, best practices, and roadmaps for benchmarking materials and reactor designs is critical to accelerate progress and lower barriers for new researchers.

In this presentation, we will discuss recent HydroGEN EMN community-based efforts in defining metrics, best practices, and gaps in STCH. In addition, we will present a brief summary of EMN nodes/capabilities as well as key conclusions from a recent questionnaire and from a recent HydroGEN Benchmarking & Protocols Workshop specifically for STCH.

11:30 AM PANEL DISCUSSION
This work presents a detailed PL spectroscopy investigation on thin nanostructured TiO\textsubscript{2} films prepared by Pulsed Laser Deposition. To selectively discern the luminescent traps, the effects of different degrees of defectivity, related to oxidizing (air) and reducing (Ar/H\textsubscript{2}) treatments, on the PL properties is considered. With both UV and green excitation, the PL emission is quenched and that of the other films exhibits a blueshift, compatible with the effect of reducing thermal treatments and the comparison between different excitation wavelengths (i.e. above and below the bandgap energy) are very limited.

The present findings confirm how PL spectroscopy can efficiently probe defect states in reduced TiO\textsubscript{2} systems, allowing a deeper understanding on the relationship between defects and photoactivity, yielding to higher performance; in this way, defects such as oxygen vacancies and Ti\textsuperscript{3+} ions are quenched and that of the other films exhibits a blueshift, compatible with the effect of reducing thermal treatments and the comparison between different excitation wavelengths (i.e. above and below the bandgap energy) are very limited.

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**ES11.02.02**

**Nanotechnological Spinel Ferrite Photoanodes for Photoelectrochemical Water Splitting**

Kristin Kirchberg\textsuperscript{1}, Stefanie Waitz\textsuperscript{2}, Songcan Wang\textsuperscript{3}, Christian Suchomski\textsuperscript{1}, Torsten Brezesinski\textsuperscript{1}, Lianzhu Wang\textsuperscript{4} and Roland Marschall\textsuperscript{5,6}; \textsuperscript{1}Justus-Liebig-University Giessen, Giessen, Germany; \textsuperscript{2}University of Bayreuth, Bayreuth, Germany; \textsuperscript{3}Georg-August-University Göttingen, Göttingen, Germany; \textsuperscript{4}The University of Queensland, Brisbane, Queensland, Australia; \textsuperscript{5}Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

Mesoporous ZnFe\textsubscript{2}O\textsubscript{4} and LiFe\textsubscript{2}O\textsubscript{4} thin film photoanodes were fabricated by sol-gel synthesis\textsuperscript{[1,2]} using a polymer-templating approach. By means of different amphiphilic diblock- and triblock copolymers, large and partly ordered mesopores are obtained after dip-coating by evaporation-induced self-assembly followed by heat treatment. Scanning electron microscopy (SEM) confirms the porous morphology, and Raman spectroscopy and XRD Rietveld analysis revealed phase pure spinel ferrite photoanodes.

Furthermore, photocurrent and Mott-Schottky measurements were performed at different pH values to determine the flat band potential and photocurrent density of the thin film photoanodes calcined at various temperatures. By varying the block-copolymers, altered pore structures of the photoanodes and their influence on photoelectrochemical performance will be discussed.

**ES11.02.03**

**Excitation Wavelength- and Medium-Dependent Photoluminescence of Reduced Hierarchical TiO\textsubscript{2} Films**

Luca Mascaretti\textsuperscript{1,2}, Valeria Russo\textsuperscript{1,2}, Giorgio Zoppellaro\textsuperscript{1,2}, Andrea Lucotti\textsuperscript{1}, Carlo S. Casari\textsuperscript{1,3}, Stephan Knerr\textsuperscript{4}, Alberto Naldoni\textsuperscript{5} and Andrea Li Bassi\textsuperscript{5}; \textsuperscript{1}Department of Energy, Politecnico di Milano, Milano, Italy; \textsuperscript{2}Regional Centre of Advanced Technologies and Materials, Palacky University Olomouc, Olomouc, Czechia; \textsuperscript{3}Center for Nanoscience and Technology - IIT@Polimi, Istituto Italiano di Tecnologia, Milano, Italy; \textsuperscript{4}Department of Chemistry, Materials and Chemical Engineering "Giauho Natta", Politecnico di Milano, Milano, Italy.

Nanostructured forms of TiO\textsubscript{2} have been extensively investigated as photoactive materials for energy-related applications, such as dye-sensitized solar cells, photocatalysis and water splitting. Annealing in reducing atmospheres has been frequently employed as an approach to increase TiO\textsubscript{2} performance; in this way, defects such as oxygen vacancies and Ti\textsuperscript{3+} sites are introduced, leading to increased light absorption, higher \emph{n}-type conductivity, and new catalytic sites with enhanced reactivity\textsuperscript{[1]}. These defects often induce a series of discrete electronic states in the bandgap with similar energies and their characterization is of pivotal importance for a deep understanding of their role in the enhancement of the material performance; this aspect is still an open topic in the current research. A powerful tool to probe such defect states is photoluminescence (PL) spectroscopy. For anatase TiO\textsubscript{2}, in particular, a broad visible emission is observed, with two main components in the green (\emph{green PL}) and in the red (\emph{red PL}) regions associated with holes and electrons in deep traps, respectively\textsuperscript{[2]}.

However, a definitive framework is still lacking: PL properties depend on the material porosity/morphology and detailed investigations concerning the effect of reducing thermal treatments and the comparison between different excitation wavelengths (i.e. above and below the bandgap energy) are very limited.

The present findings confirm how PL spectroscopy can efficiently probe defect states in reduced TiO\textsubscript{2} systems, allowing a deeper understanding on the relationship between defects and photoactivity, yielding to higher performance; this aspect is still an open topic in the current research. A powerful tool to probe such defect states is photoluminescence (PL) spectroscopy. For anatase TiO\textsubscript{2}, in particular, a broad visible emission is observed, with two main components in the green (\emph{green PL}) and in the red (\emph{red PL}) regions associated with holes and electrons in deep traps, respectively\textsuperscript{[2]}.

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The development of an efficient, stable photoanode to provide protons and electrons to the (photo)electrode remains a primary materials challenge in the establishment of a scalable technology for artificial photosynthesis. However, the absolute and relative stability and performance of different OER catalysts varies with proton density with pH. The operational conditions for the solar fuels generator is often dictated by the pH stability range of the light absorber, not the conditions optimal for OER catalysts. We have evaluated the activity and stability against corrosion of over 10,000 multi-metal oxide compositions from pH 1-13 using high-throughput electrochemical methods. The experimental and data processing methods and characteristic results are described. The Mn-Sb-O system contained compositions and structures with high acid stability and OER catalytic performance. The characterization of performance and structure of the Mn-rich alloys in the rutile oxide structure will be described. The typical photoanode architecture consists of a semiconductor light absorber coated with a metal oxide that serves a combination of functions, including corrosion protection, electrolysis, light trapping, hole transport, and elimination of deleterious surface recombination sites. We describe a high throughput investigation of the variation in performance and photo-response of individual photoanodes consisting of BiVO$_4$ coated with a sputter deposited Fe-Ce oxide film as a function of composition and adjacent metal(ll) content.

Photocatalytic water splitting is one of the potential approaches for the generation of hydrogen which can fulfill the global energy requirement [1]. But BiVO$_4$ photoanode show poor photo conversion efficiency due to poor charge transport, fast surface charge recombination and sluggish water oxidation kinetics [3]. To overcome the poor charge transport, we report formation of composite of BiVO$_4$ with modified and unmodified graphite carbon nitride (C$_3$N$_4$). In current study photocatalyst electrochemical properties of BiVO$_4$, C$_3$N$_4$ and electronic properties of Tungsten (W) metal were utilized to make a composite with enhanced Photocatalytic properties. BiVO$_4$, BiVO$_4$-C$_3$N$_4$ and BiVO$_4$-C$_3$N$_4$-W composite photo anode was prepared using facile dip coating technique. The BiVO$_4$-C$_3$N$_4$-W electrode has shown much improved photocatalytic water splitting performance at 1.23 V vs RHE, under one sun illumination on both from front and backside of electrode. In particular, the photocatalytic current density (1.2 mA.cm$^{-2}$) shown by BiVO$_4$-C$_3$N$_4$-W was about twenty times higher than pristine BiVO$_4$(0.06 mA.cm$^{-2}$). The microscopic, XRD and XPS analysis showed that BiVO$_4$ grain interaction with C$_3$N$_4$ led to formation of composite system which can efficiently suppress hole-electron pair recombination. The electrochemical impedance and cyclic voltametry measurements showed that the composite formation can lowered the interface resistance, charge transfer resistance and increased the charge donor/surface state density. Further PEC performance was corroborated with changes in band gap, crystal lattice, surface grain morphology occurred in BiVO$_4$-C$_3$N$_4$-W composite.

Reference:

**4:00 PM ES11.03.03**

**Study of Enhancement in Photocatalytic Water Oxidation Performance of Monoclinic BiVO$_4$ with Systematic Doping with Yttrium**

Umesh Prasad, Jyoti Prakash, Bruno Azeredo and AM Kannan; The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, Arizona, United States.

Photocatalytic (PEC) water splitting is one of the potential approaches for the generation of hydrogen which can fulfill the global energy requirement [1]. In developing economical and efficient photo-catalysts for water oxidation, n-type monoclinic BiVO$_4$ has been widely reported due to its favorable band gap [2]. But the photo conversion efficiency of BiVO$_4$ catalyst is relatively low due to poor charge transport, fast surface charge recombination and sluggish water oxidation kinetics [3]. In current report, BiVO$_4$ photocatalyst doped with yttrium(Y) was prepared by ultrasonic spray coating technique to overcome poor charge transport. Various percentage of Y (1,2,3,4,5 wt %) is doped in pristine BiVO$_4$ to optimize the PEC performance. The 4wt% Y doped BiVO$_4$ photo-anode has shown highest PEC photocurrent 2.20 mA.cm$^{-2}$ at 1.23 V RHE and 4.5 mA/cm$^2$ at 2 V RHE under simulated one sunlight illumination in K$_2$HPO$_4$ electrolyte. However, the photocatalytic activity of the other Y: BiVO$_4$ photo anodes were suppressed as the Y doping level decreased or increased, which could be attributed to the formation of photogenerated charge carrier recombination centers at the Y substituting sites. Here, Y$^{3+}$ dopant replaces Bi$^{3+}$ sites in BiVO$_4$ lattice to provide expanded light absorption wavelength region from 400-600nm. Further, Y: BiVO$_4$ photoanode were investigated by XRD, XPS and SEM. It was observed from Y: BiVO$_4$ that Y-doping didn't generate any impurity phases in pristine BiVO$_4$. XPS analysis showed the Y-peaks 3d$_{3/2}$ and 3d$_{5/2}$ at the binding energies 165eV and 160eV respectively, which confirm the oxidation state of Y as +3. The microscopic, XRD and XPS analysis showed that BiVO$_4$ grain interaction with C$_3$N$_4$ led to formation of composite system which can efficiently suppress hole-electron pair recombination. The electrochemical impedance and cyclic voltametry measurements showed that the composite formation can lowered the interface resistance, charge transfer resistance and increased the charge donor/surface state density. Further PEC performance was corroborated with changes in band gap, crystal lattice, surface grain morphology occurred due to Y doping in BiVO$_4$.

Reference:
Behavior of Electrochemically Generated Hydrogen Bubbles on Silicon Microwire Arrays Paul A. Kempler1, Robert H. Coridan2, Yikai Chen3 and Nathan S. Lewis1, 2; California Institute of Technology, Pasadena, California, United States; 3Chemistry, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States.

Electrochemical generation of hydrogen and oxygen during photoelectrochemical water splitting leads to the formation of gas bubbles when the concentration of dissolved gases exceeds a critical concentration in solution. Gas bubbles inhibit the performance of solar-to-fuels devices by reflecting incident sunlight and restricting mass transfer to and from catalysts. Membrane embedded microwire arrays provide a path to fully integrated solar-to-fuels devices, but the removal of gas bubbles from the underside of the device is challenging, as gravity will direct bubbles towards the photoelectrode surface. Studies on silicon-based cathodes in a variety of orientations relative to the gravitational vector will aid in understanding the opportunities and challenges associated with unassisted photoelectrochemical water-splitting at scale.

Arrays of silicon microwires were formed via photolithographic patterning and reactive ion etching and then coated with a sputtered platinum electrocatalyst layer to form cathodes which were stable in acidic media and operated at low catalytic overpotentials for hydrogen evolution. Devices were characterized via electrochemical measurements in 0.5 M H2SO4 (aq) coupled with high speed photography. The effects of the wire diameter and packing fraction on the nucleation density and break-off diameter of hydrogen bubbles as a function of current density have been characterized. All electrode designs were found to exhibit significant hydrogen bubble coverage at current densities in excess of 75 mA cm-2, but at current densities expected for solar-to-fuels devices driven by unconcentrated sunlight—less than 30 mA cm-2—bubble coverage could be suppressed by appropriate microwire array designs. The operational overpotentials of large area cathodes have been compared as a function of tilt in a downward facing orientation to assess the ability of microwire arrays to remove bubbles without assistance under operating conditions.

4:45 PM ES11.03.06

Photo-electrochemical water splitting systems at present show low performance compared to theoretical predictions. One of the reasons for this low performance is the inefficiency of oxygen evolution reaction (OER), which occurs at the semiconductor (photoanode)-electrolyte interface. Hence, for improving the performance of such water splitting systems, we need to improve the performance of the semiconductor-electrolyte interface. However, it is still unclear, what the performance limiting processes are at the interface. We present a new approach for those systems that allows for simulating - from an atomistic model - the same electrochemical data that is measured experimentally. [1] We develop a micro kinetic model for the OER by combining density functional theory (DFT) and state-space modeling. By comparing theory and experiments, the performance limiting processes at the interface can be identified.

In literature, micro kinetic modeling has been successfully used for metallic electrodes, using Butler-Volmer theory for calculation of reaction rates. [2] However, Butler-Volmer theory is only valid for metal-electrolyte interface and does not describe the charge transfer reactions at the semiconductor-electrolyte interface during water splitting process. [3] We therefore use the Gerischer theory for semiconductors in this study. Hematite (Fe2O3) – water interface is the model system used here. We choose the four step OER mechanism proposed by Rossmail et al. [4] as the electrochemical model. Based on this mechanism, mass conservation and charge balance equations are formulated. The resulting set of differential equations are represented as a state-space model (SSM); the applied potential is the input and the current density is the output. The energy of formation of the four OER intermediates at hematite surface are calculated by DFT [5] and are used to calculate the reaction rates. With this input and hematite specific parameters from the literature, electrochemical data such as current-voltage plots and electrochemical impedance spectra are simulated from the state-space model. We can also simulate the surface coverages of all intermediate species as a function of applied potential. This data is experimentally not available, but is of utmost importance for experimental studies on identification of OER intermediates. The simulated impedance from the electrochemical reactions are compared to measured impedance data from in-house experiments [1]. The simulation results are in close agreement with the experimental measurements and capture the dynamics well. Identification of performance limiting processes by comparison with experiments will be discussed. The model is generic and can be extended to study other materials and other interfaces. From a multi-scale modeling perspective, the developed model is a continuum model, which connects first principle calculations and experimental data for semiconductor-electrolyte interfaces. Further, predicting the effect of doping and cocatalyst loading on the surface of the semiconductor electrode using the model will also be discussed.

References

SESSION ES11.04: Poster Session I: Low Temperature Water Splitting Via Electrochemistry and Photoelectrochemistry
Session Chairs: Todd Deutsch and Chengxiang Xiang
Tuesday Afternoon, April 23, 2019
5:00 PM – 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES11.04.01
GaAs Nanomembranes for Solar Water Splitting Haneol Lim1, Yukun Sun2, Minjoo Lee3 and Jongseung Yoon1, 2; 1Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2Department of Electrical and Computer Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois, United States; 3Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States.

Despite their outstanding photovoltaic performance and record-high solar-to-hydrogen efficiency, the high production cost and limited photoelectrochemical stability of III-V compound semiconductors prohibit their practical application in solar-driven photoelectrochemical water splitting. Here we present a novel strategy for III-V photoelectrodes that can overcome these obstacles via printing-based assemblies of surface-engineered, epitaxially-grown nanomembranes. Ultrathin (i.e. emitter + base = 300 nm) GaAs photocathodes having a buried pn-junction are released from the growth wafer and printed onto a non-native, transparent substrate to form integrated bifacial photocathodes for the hydrogen evolution half-reaction of solar water splitting. Hexagonally periodic TiO2 nanoposts are incorporated into the light-absorbing interface of ultrathin GaAs to maximize the light absorption, while the n-type ohmic metal, protection layer, and co-catalyst are deposited on the reactive interface to optimize the catalytic efficiency and stability. The resulting bifacial GaAs photocathodes with nanoplanar light management exhibit significantly enhanced saturated current density (from -11.7 mA cm-2 to -16.3 mA cm-2) and diagnostic electrode efficiency (from -8.6% to -11.3%) compared to the bare GaAs photocathodes without TiO2 nanoposts, under AM1.5G solar illumination in aqueous sulfuric acid (0.5 M H2SO4).

ES11.04.02
Piezoelectric-Photoelectrochemical Characteristics of ZnO Nanopyramids for Sono-Assisted Water Splitting Yaqiong Li1, 2, Taehoon Lim2, Kichang Jung3, 4 and Alfredo A. Martinez-Morales4; 1Materials & Science Research, University of California, Riverside, Riverside, California, United States; 2College of Engineering - Center for Environmental Research and Technology, University of California, Riverside, Riverside, California, United States; 3Department of Chemical and Environmental Engineering, University of California, Riverside, Riverside, California, United States.

To date, there has been intense research in zinc oxide (ZnO) nanostructures in terms of the variety of morphologies that can be achieved and the availability of low-cost synthesis methods. ZnO is a versatile photo-responsive material which can be used as photocatalyst and photoelectrode for solar cells (e.g. perovskite solar cells). The photocatalytic activity of ZnO can be further enhanced by the extra polarization from the piezoelectric operation under external mechanical forces. Due to their low stability against mechanical stress.
one-dimensional ZnO such as nanowires and nanorods have inherent limitations for sono-assisted water splitting applications. In this work, we investigate pyramidal ZnO structures for piezoelectric-photocatalytic devices by utilizing their higher mechanical stability and photocatalytic activity. The surface of pyramidal ZnO with (112) crystal plane has higher surface energy and photocatalytic activity.

To achieve the ZnO nanopyramid we utilize a modified crystal growth method by adjusting the reaction kinetics and fluid dynamics during chemical vapor deposition (CVD). Synthesis under different experimental parameters such as reaction temperature, reactor design, reaction pressure, and gas ratio are carried out. The morphology is controlled by adjusting experimental parameter and the effects of crystal growth conditions on the piezoelectric-photocatalytic properties are also investigated. The morphology, crystal structure, and optical/electrical properties of synthesized ZnO are characterized by the scanning electron microscopy, X-ray diffraction analysis, and optical spectroscopies, respectively. The piezoelectric and photocatalytic properties are characterized by piezoelectric force microscopy and potentiostat measurements, respectively. The enhanced performance of photocatalytic water splitting is tested under the presence of mechanical forces in the form of ultrasonic waves.

ES11.04.03
Low and High -Temperature Electrolysis, Solar and thermochemical Water Splitting Materials Characterization and Development at Berkely Lab Under the HydroGEN Consortium Nemania Danilovic, Frances Houle, Ahmet Kusoglu, Francesca Maria Toma, Mike Tucker, Lin-Wang Wang and Adam Weber; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The HydroGEN consortium brings together unique National Laboratory experts and tools (nodes) with researchers developing advanced water splitting materials in a variety of technologies: Low and High -Temperature Electrolysis (LTE/HTE), Photoelectrochemical (PEC) and Solar-Thermochemical (STCH) Water Splitting. Lawrence Berkekey National Laboratory is a HydroGEN partner lab and has participated in 9 projects since 2018. This poster will highlight -Berkley Lab capabilities and expertise available to researchers in LTE, HTE, PEC and STCH fields -Our collaborative work performed with our partners in LTE, HTE and PEC in the last year -Benchmarking LTE, PEC and HTE materials performance -Tackling big scale problems in LTE, PEC and HTE through multi-node, multi-institution projects "supermodes"

ES11.04.04
CuGaSe2/Zn1−xMgO Photocathodes for Photocatalytic Water Splitting Impar S. Khan¹, Karen Heinseleman¹, Christopher Muzzillo¹, James L. Young², Todd G. Deutsch³, Andriy Zakutayev⁴ and Nicolas Gaillard⁵; National Renewable Energy Laboratory, Golden, Colorado, United States; ¹University of Hawaii, Honolulu, Hawaii, United States.

CuGaSe₂ is a promising absorber material for photocatalytic (PEC) water splitting due to its suitable wide band gap and durability in electrolyte solution. Zn₁₋ₓMgO is a potential buffer layer for the CuGaSe₂ absorber, because of its tunable conduction band offset as a function of Mg concentration. Zn₁₋ₓMgO thin film is deposited on the evaporated CuGaSe₂ absorber using combinatorial RF sputtering. Prior to the buffer layer deposition, the absorber is treated in Ca²⁺ containing solution. The quality of the CuGaSe₂/Zn₁₋ₓMgO interfaces as a function of varying Mg is studied based on solid state photovoltaic device performance. PEC performance of the device is characterized in three electrode configuration with SiO₂/Mo/CuGaSe₂/Zn₁₋ₓMgO as the photocathode, Pt counter electrode, and a reference electrode. To quantify the device performance in relation to the Mg content in the buffer, chopped-light current–voltage (CLIV) measurement is performed using a scanning droplet cell measurement system. The results of these experiments facilitate the understanding of the CuGaSe₂/Zn₁₋ₓMgO photocathode interfaces, and application of CuGaSe₂ absorbers for PEC water splitting. This work was performed as part of the HydroGEN EMN between National Renewable Energy Laboratory (NREL) and University of Hawaii, with support from the Combinatorial (A. Zakutayev), Chalcopyrite (C. Muzzillo), and PEC (T. Deutsch) nodes at NREL.

ES11.04.05
Measurement of the IPCE of Photocatalytic Electrodes Using a Pump-and-Probe Method Martin Velazquez-Rizo², Jan Diego Trelles-Molina²,¹, Liang Zhang¹, Leticia Castrejon Barron¹, Daisuke Iida¹ and Kazuhiro Okawa¹; ¹Computer, Electrical and Mathematical Science and Engineering (CEMSE) Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; ²Monterey Institute of Technology and Higher Education, Monterey, Mexico.

We demonstrated that a pump-and-probe method to measure the incident photon-to-current efficiency (IPCE) is reliable. We confirmed that the photocurrent of a catalytic photocathode is better described through the IPCE obtained using this method than with the IPCE obtained using only monochromatic irradiation. Commonly, the IPCE is measured through its conventional method, where the photoabsorption device is irradiated with monochromatic light and the photocurrent generated is recorded [Hwang, et al. Nanotechnology, 24, 055401 (2013)]. Then, the IPCE is derived from the response current, the applied optical power and the wavelength of the monochromatic light. The IPCE spectra obtained with this method is expected to diverge from realistic values, fundamentally because of the changes in the band diagram of photocathodes when they are excited. During the water photoelectrolysis reaction, photocathodes are irradiated with a considerable amount of optical power. Such excitation takes them to a non-equilibrium thermodynamic state, modifying not only their band structure but their carrier dynamics as well. Therefore, the method we utilized finds out the IPCE of a photocatalytic cell once its photocathode is already at a given excited state. To show the scope of this method, we characterized the IPCE of a photocatalytic cell with a SiO₂/CuGaN photocathode [Hayashi, Okawa, et al. J. Appl. Phys. 51, 112601 (2012)]. It was irradiated with a power density of 100 mW/cm² using a Xe lamp, which is the same power density used for the photoelectrochemical H₂/O₂ production. The IPCE values were calculated from the additional photocurrent induced by the monochromatic probe light. The IPCE spectrum was measured in different locations of the photocathode, and the total photocurrent was obtained by integrating the convolution of the Xe lamp radiation spectrum and the IPCE over the photoabsorption range and the geometrical area of the photocathode. The base photocurrent of the photocathode was L × 0.45 mA/cm². Using the IPCE obtained through the conventional method, the photocurrent calculated was as large as 3.01 mA/cm² (≈6.69 L). On the other hand, the value calculated using the IPCE from the pump-and-probe method was as good as 0.57 mA/cm² (≈1.27 L). Thus, using the pump-and-probe method, we obtained a calculated photocurrent value almost equal to the base photocurrent. This result indicates that the IPCE values obtained using the pump-and-probe method drastically improved the description of the photocurrent behavior of photocathodes. This measuring technique will help to characterize photocatalytic cells more reliably, and it also gives an insight into the differences in the band structure of semiconductors when they are in a non-equilibrium state.

ES11.04.06
Improvement in Performance of CuO Photocathode for Hydrogen Evolution in Solar Water Splitting Kichang Jung¹,², Taehoon Lim³, Hyojung Bae³, Jun-Seok Ha¹,⁴ and Alfredo A. Martinez-Morales¹,⁵, ¹Chemical and Environmental Engineering, University of California, Riverside, Riverside, California, United States; ²College of Engineering Center for Research & Technology, University of California, Riverside, California, United States; ³Optoelectronics Convergence Research Center, Chonnam National University, Gwangju, Korea (the Republic of); ⁴School of Chemical Engineering, Chonnam National University, Gwangju, Korea (the Republic of); ⁵Materials Science and Engineering Program, University of California, Riverside, Riverside, California, United States.

In this work, we study the performance of CuₐO as a photocathode for photoelectrochemical water splitting. The morphology of the CuO is engineered to improve the hydrogen generation efficiency through the enlargement of the surface area and increased light absorbance. The nanostructured CuO is synthesized by a two-step method. First, a Cu layer is deposited by e-beam evaporator onto FTO. Second, the CuO nanostructure film is obtained via a solution and thermal oxidation method under nitrogen environment. Due to the p-type semiconductor properties of CuO, the synthesis film can be used as a catalyst for the reduction reaction. This research shows improvement in the photoelectrochemical efficiency of CuO photocathodes by preventing the formation of unreduced Cu layer between CuO and conductive substrate (FTO). Specifically, the effect of unreduced Cu layer is investigated. CuO samples are synthesized with the same surface morphology, but exhibit different unreduced Cu layer thickness between CuO and FTO. The fully reacted CuO photocathode shows an enhanced photocurrent density and improved efficiency in hydrogen evolution compared to CuO with unreduced Cu. The enhanced photocatalytic performance of the photocathode without a trace of unreduced Cu layer is attributed to the reduction in charge recombination resulting from the full oxidation of the Cu layer. Experimentally, it is confirmed that unreduced Cu significantly reduces carrier lifetime and negatively affects the photoelectrochemical performance of the photocathode. The elimination of the unreduced Cu layer leads to higher photocurrent density. Morphology of CuO is characterized by scanning electron microscopy. Crystallinity of the samples is analyzed by X-ray diffraction. Absorbance is measured by ultraviolet-visible-near infrared spectrophotometry. The electrochemical properties of the synthesized materials in the electrolyte are analyzed by measuring current density versus voltage and electrochemical impedance spectroscopy.
Photoelectrochemical Characterization of Cuprous Oxide (Cu₂O) Thin Films Deposited by Chemical Bath Deposition (CBD)

Cuprous oxide (Cu₂O) is a p-type semiconductor with a direct band gap of about 2.0-2.7 eV and high absorption coefficient. Due to its outstanding photoelectronic properties, natural abundance, non-toxic nature, and simple preparation procedures, Cu₂O has generated interest in various applications, such as the conversion of solar energy into electrical or chemical energy, photochemical decomposition of water into O₂ and H₂ under visible-light irradiation, photocatalyst for degradation of organic contaminants, as hole transporting material in device photovoltaic technology, for gas sensing and magnetic storage. Cu₂O thin films are commonly deposited by thermal oxidation of copper thin films, which previously are deposited by sputtering or evaporation. Thermal oxidation is an expensive technique because of high temperatures and consequently the wasting of energy. In the other hand CBD is an economic, easy and scalable deposition technique, which is not well studied for Cu₂O thin films deposition.

We report an easy and direct CBD method for Cu₂O thin films. We have studied the effect of thickness on the optical, structural, morphological, electrical and photoelectrochemical properties. The thin films were analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), energy dispersive spectroscopy (EDS), UV-vis spectroscopy, electrically and photoelectrochemical characterized by Electrochemical impedance spectroscopy. The combined PV-PEC cell can benefit not only from the high oxidation potential of ZnO NRs but also from the visible range light absorption of Cu₂O to smoothen the p-n junction interface. We for the first time produced p-n homojunction Cu₂O Z-Scheme PV-PEC Cells for the Low Bias Photoelectrochemical Water Splitting Enabled by NiFe-Layered Double Hydroxide Co-Catalyst. Scientific Reports, 6., 1.=-Qi, H., Wolfe, J., Fichou, D., & Chen, Z. (2016). Cu₂O Photocathode for water splitting—a critical review. Energy & Environmental Science, 8(3), 751-759.

Enhanced Photoelectrochemical Responses of ZnO NR/p-n Cu₂O Z-Scheme PV-PEC Cells

One proposed integrated solar water splitting device involves two ion-exchange membrane-embedded, semiconducting micro-/nanowire arrays electrically connected as a tandem. Such an electrical connection must be optically transparent, ion permeable, and adhere to each membrane-embedded array. A composite Naftion-Poly(3,4-ethylenedioxythiophene)-polyethylene sulfonate (PEDOT:PSS) film possesses excellent adhesion and charge transport properties while being more transparent than PEDOT:PSS alone. Understanding the phase-separation behavior between conductive and non-conductive domains via PeakForce Tunneling Atomic Force Microscopy (PF-TUNA) enables insight towards the Naftion-PEDOT interactions that explain bulk electrical properties. A percolative network of conductive PEDOT domains held by a Naftion:PSS bulk enable electron conduction while maintaining the mechanical stability and proton conducting properties of Naftion. Addition of DMSO reduces these domain sizes from μm to nm scale, producing a dramatic >10⁴-fold increase in lateral conductivity. Nanoscale current-voltage sweeps probe the spatial variations of ionic behavior that lead to macro-scale contact resistance at composite/p-Si interfaces. The measured composite properties are input into a sensitivity analysis that guides device design via load-line analysis of a model tandem water splitting device.

Enhanced Photoelectrochemical Responses of Naftion-PEDOT:PSS Composite for Tandem Microwire Array Solar Water Splitting Devices

One proposed integrated solar water splitting device involves two ion-exchange membrane-embedded, semiconducting micro-/nanowire arrays electrically connected as a tandem. Such an electrical connection must be optically transparent, ion permeable, and adhere to each membrane-embedded array. A composite Naftion-Poly(3,4-ethylenedioxythiophene)-polyethylene sulfonate (PEDOT:PSS) film possesses excellent adhesion and charge transport properties while being more transparent than PEDOT:PSS alone. Understanding the phase-separation behavior between conductive and non-conductive domains via PeakForce Tunneling Atomic Force Microscopy (PF-TUNA) enables insight towards the Naftion-PEDOT interactions that explain bulk electrical properties. A percolative network of conductive PEDOT domains held by a Naftion:PSS bulk enable electron conduction while maintaining the mechanical stability and proton conducting properties of Naftion. Addition of DMSO reduces these domain sizes from μm to nm scale, producing a dramatic >10⁴-fold increase in lateral conductivity. Nanoscale current-voltage sweeps probe the spatial variations of ionic behavior that lead to macro-scale contact resistance at composite/p-Si interfaces. The measured composite properties are input into a sensitivity analysis that guides device design via load-line analysis of a model tandem water splitting device.

Synthesis of Graphene-Carbon Nanotube Composites Functionalized with TiO₂

Hybrid organic photoelectrochemical (HOPEC) water splitting is gaining momentum in the field of solar conversion technologies. It bridges solar-powered hydrogen production with convenient and scalable fabrication techniques through earth-abundant materials and promising performances. Mirroring the development of Organic Photovoltaics, devices based on organic semiconductors require a careful understanding of their working mechanisms as well as dedicated material research. Hybrid photoelectrodes have been able so far to deliver either high photocurrent performances or long operational lifetime. The goal is to combine these results in a single high-performing and long-lasting architecture. The performance of the device relies on the dynamics occurring across various interfaces, starting from charge separation within the bulk heterojunction (BHJ) up to hydrogen evolution in contact with the electrolyte. As demonstrated, selective contacts play a major role in maximizing the result and represent the key factor to combine stability and efficiency. At these interfaces a delicate balance of energetic, morphologic and optical properties is needed to promote lossless charge extraction. Herein materials belonging to the classes of metal oxides, organic compounds and transition metal chalcogenides are tested in the role of hole selective layers (HSL). Their performances are tuned acting on their morphology at the nanoscale to optimize the interaction with the organic BHJ and the back contact. Several deposition techniques are employed to obtain thin films exerting high control on their properties. To further increase the performances, with remarkable gain in photovoltaic, we moved toward high performing organic semiconductors, aiming to replace the state-of-the-art P3HT:PCBM BHJ. Among these, photoelectrodes employing PCDTBT:PC70BM delivered excellent performances, with a noteworthy photocurrent onset potential of 0.85 V vs RHE, surpassing the actual 0.6 V vs RHE benchmark achieved with P3HT:PCBM. With the aid of AFM-Kelvin Probe, we collected work function data to have an estimate of the energetic structure of the HSL and of the HSL/BHJ coupling. UV-Vis spectra have been acquired to assess the high transparency of HSL and to integrate them the BHJ. Finally, we carry out the photoelectrochemical characterization of hybrid photoelectrodes employing the most promising hole selective layer candidates and novel BHJ. These architectures deliver photocurrents higher than 3.5 mA/cm² over several hours of continuous operation. Furthermore, taking advantage of the properties of PCDTBT:PC70BM, we successfully realized photocathodes which do not require any post-fabrication thermal treatment. With this work we set the development of low temperature, stable and high-performing hydrogen evolving photocathodes as near-future goal.


Synthesis of Graphene-Carbon Nanotube Composites Functionalized with TiO₂

Harold J. Fu1, 2, Alessandro Mezzetti1, Emilio Palomares3 and Fabio Di Fonzo1; 1Istituto Italiano di Tecnologia, Milano, Italy; 2Physics, Politecnico di Milano, Milano, Italy; 3Institut Català d'Investigació Química, Tarragona, Spain.

Hybrid organic photoelectrochemical (HOPEC) water splitting is gaining momentum in the field of solar conversion technologies. It bridges solar-powered hydrogen production with convenient and scalable fabrication techniques through earth-abundant materials and promising performances. Mirroring the development of Organic Photovoltaics, devices based on organic semiconductors require a careful understanding of their working mechanisms as well as dedicated material research. Hybrid photoelectrodes have been able so far to deliver either high photocurrent performances or long operational lifetime. The goal is to combine these results in a single high-performing and long-lasting architecture. The performance of the device relies on the dynamics occurring across various interfaces, starting from charge separation within the bulk heterojunction (BHJ) up to hydrogen evolution in contact with the electrolyte. As demonstrated, selective contacts play a major role in maximizing the result and represent the key factor to combine stability and efficiency. At these interfaces a delicate balance of energetic, morphologic and optical properties is needed to promote lossless charge extraction. Herein materials belonging to the classes of metal oxides, organic compounds and transition metal chalcogenides are tested in the role of hole selective layers (HSL). Their performances are tuned acting on their morphology at the nanoscale to optimize the interaction with the organic BHJ and the back contact. Several deposition techniques are employed to obtain thin films exerting high control on their properties. To further increase the performances, with remarkable gain in photovoltaic, we moved toward high performing organic semiconductors, aiming to replace the state-of-the-art P3HT:PCBM BHJ. Among these, photoelectrodes employing PCDTBT:PC70BM delivered excellent performances, with a noteworthy photocurrent onset potential of 0.85 V vs RHE, surpassing the actual 0.6 V vs RHE benchmark achieved with P3HT:PCBM. With the aid of AFM-Kelvin Probe, we collected work function data to have an estimate of the energetic structure of the HSL and of the HSL/BHJ coupling. UV-Vis spectra have been acquired to assess the high transparency of HSL and to integrate them the BHJ. Finally, we carry out the photoelectrochemical characterization of hybrid photoelectrodes employing the most promising hole selective layer candidates and novel BHJ. These architectures deliver photocurrents higher than 3.5 mA/cm² over several hours of continuous operation. Furthermore, taking advantage of the properties of PCDTBT:PC70BM, we successfully realized photocathodes which do not require any post-fabrication thermal treatment. With this work we set the development of low temperature, stable and high-performing hydrogen evolving photocathodes as near-future goal.
Recently, there have been intense efforts in the exploration of innovative solar cell structures with high performance and cost-effective manufacturing methods. One of the alternatives is the use of carbon nanotubes in photoelectrochemical cells, as an effective strategy to increase the efficiency of the devices. For this purpose, this work aims to use functionalized multiwalled carbon nanotubes (mwcnt) with titanium dioxide nanoparticles (TiO2) by a mechanical-thermal process, and then with a spray method to obtain a hybrid material of bilayer graphene and mwcnt functionalized with TiO2 characterizing the structural, chemical and optical properties of the resulting composites. In a first stage a sintering process is applied, varying the temperatures, with the aim of introducing vacancies in the outer layer of the carbon nanotubes. The mwcnt are subjected to a mechanical process adding TiO2 and finally by the method of spraying of bilayer graphene and mwcnt functionalized with TiO2 obtain a complex material.

ESI1.04.13
Strategies for Minimizing Reflection by Electro catalysts Integrated on Silicon Microwire Array Photocathodes
Paul A. Kempler, Sisir Yalamanchili, Kimberly Papadantonakis and Nathan S. Lewis; California Institute of Technology, Pasadena, California, United States.

High aspect ratio, microstructured photocathodes allow for the integration of reflective and opaque electro catalysts with semiconducting light absorbers, while avoiding losses to the maximum photocurrent density. Microwire and microarray arrays have been fabricated from p-type Si and decorated with thick films of electrochemically deposited CoP or sputtered Pt to prepare photocathodes for the generation of H2 from 0.5 M H2SO4 (aq). P-Si-CoP microwire and microcane arrays produced photocurrent densities of ~10 mA cm–2 at potentials that were ~130 mV more positive than optimized planar p-Si/CoP devices. Champion p-Si/CoP microwire array devices exhibited ideal regenerative cell solar-to-hydrogen efficiencies > 3%, and were primarily limited by the photovoltage of the p-Si/CoP junction. Thick (~16 nm) layers of Pt or CoP deposited onto n- p-Si microcane arrays yielded light-limited photocurrent densities of ~ ~32 mA cm2, constituting a reduction in light-limited photocurrent density of 6% relative to bare Si µ-cone-array photocathodes, while maintaining high fill factors and low overpotentials for H2 production.

ESI1.04.14
Efficient Solar to Hydrogen Conversion Using Morphology-Controlled Sb2Se3 Light Absorbers in Neutral Electrolytes
Jaemin Park, Woo seok Yang, Yujung Oh, Ji eawn Tan, Hyungs oo Lee, Ramireddy Boppella and Jooho Moon; Yonsei University, Seoul, Korea (the Republic of).

For practical hydrogen production via photoelectrochemical (PEC) water splitting, low-cost photocathodes that can efficiently operate in neutral electrolytes should be developed. Herein, we present novel solution-based synthesis method enabling the morphology variation of Sb2Se3 light absorber, which are nontoxic, low bandgap and earth-abundant materials. The morphology of Sb2Se3 films varies from dense particulate planar film to 1-dimensional nanowire-stacked film upon modifying the Sb and Se molar ratio in the precursor ink. The resulting Sb2Se3 films have identical composition and bandgap value regardless of initial precursor ratios. The formation mechanism was elucidated by analyzing Se-Sb precursor ink using liquid Raman spectroscopy. The effects of morphology and crystallographic orientation on the electrical and consequently the charge transport properties of Sb2Se3 photocathodes are investigated by conductive atomic force microscopy. Sequential deposition of CdS as a buffer layer with TiO2 and Pt on the morphology controlled Sb2Se3 film enables us to reduce a band offset between the Sb2Se3 and TiO2, achieving an enhanced onset potential. An onset potential of 0.55 V versus reversible hydrogen (RHE) electrode was obtained with 11 mA cm–2 at 0 V versus RHE under 1.5 global illumination in a neutral electrolyte (pH 6.5). Furthermore, stable hydrogen production over ~3 h was observed during the course of photocurrent generation by gas chromatography, demonstrating the promising potential of the proposed Sb2Se3 photocathodes as efficient PEC water-splitting devices.

SESSION ESI1.05: High Efficiency PEC Materials and Devices I
Session Chairs: Nicolas Gaillard and Shu Hu
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 121 C

8:15 AM *ESI1.05.01
Development of Catalytic Coatings for H2-Producing Photocathodes in Solar Water-Splitting
Thomas Jaramillo1,2,3, Chemical Engineering Dept., Stanford University, Stanford, California, United States; 2Photon Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 3SUNCAT Center for Interface Science and Catalysis, Stanford and SLAC, Stanford, California, United States.

The vast majority of fuels and chemicals that are produced and consumed across the globe today are derived from fossil fuels: oil, coal, and natural gas. This is true of H2 as well, with annual production rate of over 60 billion kg/year, predominantly used in petroleum refining and in fertilizer production. Developing new, sustainable routes to H2 production using renewable resources (e.g. wind and solar) could play an important role in decarbonizing energy, and motivate new uses of H2 as a fuel itself and/or reducing agent for lower-carbon footprint processes. Solar-based water-splitting is a promising route to sustainable H2. This talk will focus on photoelectrochemical (PEC) water-splitting processes, with a focus on photocathodes. To achieve a cost-effective process, ambitious targets involving efficiency, durability, and low-cost must be reached. This talk will describe efforts to develop catalyst materials and associated coatings capable of providing high activity and extended durability to photovoltaic-grade solar-absorbing materials, including silicon, chalcogenide semiconductors, and III-V materials.

8:45 AM *ESI1.05.02
Photovoltaic-Photoelectrochemical Tandem Systems for High-Efficiency Stand-Alone Solar Hydrogen Generation
Siva Karuturi, Australian National Univ, Canberra, Australian Capital Territory, Australia.

Achieving efficient hydrogen evolution in water using solar light in a stand-alone system without any external bias is a highly desirable but difficult target. Ever since the first report of sunlight induced water splitting using a TiO2 electrode four decades ago, photoelectrochemical (PEC) water splitting has been intensely investigated using various semiconductor photocathodes. However, the main requirement for a photocathode in a PEC cell to induce spontaneous hydrogen evolution is the availability of a semiconductor with an appropriate bandgap of approximately 2.5 eV, having a conduction band that is sufficiently negative for H2 evolution and a valence band that is sufficiently positive for O2 evolution. Unfortunately, devices capable of spontaneous gas evolution are inefficient because the photocathodes with a bandgap of around 2.5 eV absorb only a limited portion of the solar spectrum and require an additional bias for overcoming overpotentials.4 One approach to solve this problem of single semiconductor PEC cells is the use of a tandem configuration. In particular, a photocathode combined with an appropriate photovoltaic (PV) cell with complementary absorption ability can harvest a broad part of the solar spectrum and deliver a high solar to hydrogen conversion efficiency.5

After introducing the PV-PEC approach for unbiased hydrogen evolution, I will present our work on perovskite solar cell assisted CdS photoanode. The tandem PV-PEC device consisting CdS/TiO2 photoanode as a top absorber and encapsulated perovskite solar cell as a bottom absorber was developed on a double-side conducting glass using a facile and integrated fabrication process. The fabrication of the integrated device has been achieved by using a combination of solution processing and atomic layer deposition techniques. A remarkable highest photocurrent density of 8.2 mA/cm2 was obtained for unassisted solar hydrogen generation under AM1.5 G illumination using 0.25 M Na2S and 0.35 M Na2SO3 as an electrolyte.4 Next, I will present our recent work on tandem perovskite assisted silicon photoanodes. Highly efficient buried junction n-Si based photocathodes were developed by decoupling light harvesting and hydrogen evolution reactions and breaking the tradeoff between light harvesting and light blocking catalysts. Highly efficient transparent perovskite cathodes with appropriate bandgap were developed as a top absorber. The proposed device satisfies the critical requirement of an efficient tandem configuration by providing complementary light absorption with high optical transparency to long wavelength photons and strong PEC conversion from short wavelength photons. Using this configuration, we achieved an unprecedented ~17% solar-to-hydrogen conversion efficiency for unbiased solar water splitting.5

References:
Recently, a ternary protective coating of manganese-alloyed titanium oxide, (Ti,Mn)O, into an otherwise insulating TiO$_2$ sites help stabilize key intermediates and reduce barrier for O-O coupling for water oxidation; and ii) local electron accumulation at the buried interfaces boosted hydrogen separation and activity improvement. Two new phenomena were observed at the interfaces of few-nm ALD oxides and their coated electrocatalysts: i) three dimensional active microscopy and spectroscopy. On the other hand, the intermediate band induced electronic interactions at the nano-interface with underlying (photo-)electrodes, for charge mobility and have resulted in some of the highest efficiency photoelectrodes. However, these materials are generally very susceptible to corrosion as photoanodes in strong acidic media. Intermediate-band oxides with tunable transport energy levels can serve as chemically-stable, transparent conductive protective layers for photoelectrochemical water splitting at scale. They have shown to promote charge separation and/or charge transport to surface-attached co-catalysts or intermediates at specific electrochemical potentials, practically interfacing the otherwise unstable light absorbers with strong acid or base and protecting them against corrosion. The initial re-discovery of “leaky” TiO$_2$ films to protect Si PEC electrodes for fuel generation. However, a wide variety of performances have been obtained from ALD TiO$_2$ coated with metal oxide protection layers. Finally, we present solid-state techniques and theoretical modeling used by our team to identify possible pitfalls in these material systems and discuss potential paths for improvement.

SESSION ES11.06: Stability of PEC Materials I

Session Chairs: Nicolas Guillard and Shu Hu

Wednesday Morning, April 24, 2019

PCC North, 100 Level, Room 121 C

10:30 AM *ES11.06.01
Multi-Functional Intermediate-Band Oxides for Photoelectrochemical and Electrochemical Water Splitting Shu Hu; Chemical & Environmental Engineering, Yale University, New Haven, Connecticut, United States.

Intermediate-band oxides with tunable transport energy levels can serve as chemically-stable, transparent conductive protective layers for photoelectrochemical water splitting at scale. They have shown to promote charge separation and/or charge transport to surface-attached co-catalysts or intermediates at specific electrochemical potentials, practically interfacing the otherwise unstable light absorbers with strong acid or base and protecting them against corrosion. The initial re-discovery of “leaky” TiO$_2$ films to protect Si PEC electrodes for fuel generation. However, a wide variety of performances have been obtained from ALD TiO$_2$ coated with metal oxide protection layers. Finally, we present solid-state techniques and theoretical modeling used by our team to identify possible pitfalls in these material systems and discuss potential paths for improvement.

SESSION ES11.06: Stability of PEC Materials I

Session Chairs: Nicolas Guillard and Shu Hu

Wednesday Morning, April 24, 2019

PCC North, 100 Level, Room 121 C

11:00 AM *ES11.06.02
Investigation of the Photocorrosion of GaP and GaSbP III-V Photoanodes in Acid with In Situ UV/vis Spectroscopy Sahar Pishgar1, Gautam Gupta2, Gianmini Sumanasekera1 and Joshua M. Spurgeon1; 1Conn Center for Renewable Energy, University of Louisville, Louisville, Kentucky, United States; 2University of Louisville, Louisville, Kentucky, United States.

Semiconductors perform a critical role in photoelectrochemical processes for the conversion of solar energy into fuels. The III-V semiconductors, such as GaP, typically have high mobilities and have resulted in some of the highest efficiency photoelectrodes. However, these materials are generally very susceptible to corrosion as photoanodes in strong acidic or alkaline solutions under illumination or at applied bias. Herein, we investigate and quantify corrosion of n-GaP and a related novel ternary alloy, GaSbP, at applied bias and under illumination in strong acidic electrolyte. In situ UV/vis spectroscopy measurements, along with inductively coupled plasma mass spectroscopy (ICP-MS) were utilized to detect the dissolved semiconductor species at various operating conditions and quantify the faradaic efficiency of the corrosion reaction. Ultimately, surface protection strategies like atomic layer deposition of TiO$_2$, will be applied to probe their consequences on the semiconductor corrosion as a function of the deposition parameters.

11:15 AM *ES11.06.03
Metastable Intermediates in Amorphous Titanium Oxide—A Hidden Role Leading to Ultra-Stable Photoanode Protection Lazarus N. German1, Ynanho Yu1,2, and Xuong Wang1, 1University of Wisconsin-Madison, Madison, Wisconsin, United States; 2Harvard University, Cambridge, Massachusetts, United States.

Among many functional materials, amorphous metal oxides, particularly the thin-film morphology synthesized by atomic layer deposition (ALD), are critical components in many modern energy systems, such as batteries,[1–2] catalysts,[3–9] solar cells,[10–13] and photoelectrochemical (PEC) electrodes.[14–16] One representative example is the use of ALD amorphous TiO$_2$ films to protect Si PEC electrodes for fuel generation. However, a wide variety of performances have been obtained from ALD TiO$_2$ by varying the Ti precursor, growth
temperature, and thickness despite a longstanding, yet likely overlooked expectation that ALD films are homogeneous.\cite{10} Our recent observations have shown structural homogeneities in amorphous ALD TiO$_2$ films identified as metastable intermediates: kinetically trapped structures between the metastable amorphous phase and the equilibrium crystalline phase.\cite{11,12} These intermediates enable new and enhanced properties by which their presence significantly change the performance of the overall film. Metastable intermediates represent a nonequilibrium state of matter that impose profound impacts to materials properties beyond our understandings of monolithic and equilibrium systems. We have discovered and hidden metastable intermediates in amorphous TiO$_2$ thin films and their critical role in electrochemical damage. These intermediates have a non-bulk crystal-like structure and exhibit significantly higher electrical conductivity than both the amorphous and the crystalline phases. When these TiO$_2$ films are applied to protect Si PEC photoanodes, the intermediates can induce localized high electrochemical currents that largely accelerate the etching of the TiO$_2$ film and the Si electrode underneath. The intermediates can be effectively suppressed by raising their nucleation barrier via reducing the film thickness from 24 to 2.5 nm. The homogeneous amorphous TiO$_2$-film-coated Si photoanodes achieved more than 500 h of PEC water oxidation at a steady photocurrent density of over 30 mA/cm$^2$.

These results reveal an additional pathway for optimizing the performance of amorphous oxides grown by ALD: controlling the phase composition of the amorphous and intermediate phases is crucial for optimizing the performance of oxide protected electrodes. In addition to thickness, manipulating other deposition parameters such as temperature, precursor choice, pulse and purge times, and doping offer multiple avenues for achieving greater protection performance by impeding the formation of intermediates.

References:


11:30 AM ES11.06.05 Photoelectrochemical Hydrogen Generation from Water Using GaN with Fe$_3$O$_4$ as Cocatalyst Martin Velazquez-Rizzo, Fumio Ito, Daisuke Iida and Kazuhiro Ohkawa, Electrical and Computer and Mathematical Science and Engineering (CEMSE) Division, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; Faculty of Science, Tokyo University of Science, Tokyo, Japan.

We report for the first time the fabrication of a photoelectrode using a thin film GaN homostructure loaded with Fe$_3$O$_4$ as a cocatalyst and its successful photoelectrochemical (PEC) hydrogen gas generation from water. For the PEC characterization of the Fe$_3$O$_4$/GaN photoelectrode, it was irradiated using a Xe arc lamp with a power density of 100 mW/cm$^2$ for three hours. After this characterization, the photoelectrode did not show signals of photo-corrosion or degradation. A photoelectrode with the same GaN homostructure but using NiO as cocatalyst [Hayashi, Ohkawa, et al., Jpn. J. Appl. Phys. 51, 112601 (2012)] was also characterized under the same conditions to compare the PEC performance of both structures. The Fe$_3$O$_4$/GaN photoelectrode exhibited a stable H$_2$ generation rate of 40.6 μmol/(cm$^2$·h) and a light-to-hydrogen energy conversion efficiency of 2.6%, which is higher than the value of 2.3% found for the NiO/GaN photoelectrode. In addition, the surface of the Fe$_3$O$_4$/GaN photoelectrode was characterized using electron microscopy and energy-dispersive X-ray spectroscopy (EDS).

The thin film GaN homostructure was grown on a c-plane patterned sapphire substrate by metalorganic vapor phase epitaxy and consisted of (top to bottom) unintentionally doped (undoped)-GaN (100 nm)/n-GaN (Si-doped, n=3x10$^{18}$ cm$^{-3}$), 3 µm)/GaN (2 µm). The Fe$_3$O$_4$ cocatalyst was deposited through the spin coating of a metalorganic decomposition solution containing 3 wt% of Fe$_3$O$_4$. The PEC characterization of the photoelectrode was performed using a Pt wire as a cathode, with both electrodes immersed in 1 M NaOH solution and without applying any external electrical bias between the electrodes. The gas volume generated at the cathode and the photocurrent between the electrodes were recorded during the PEC characterization. The gas was characterized using gas chromatography to verify its H$_2$ content.

The observations performed through scanning electron microscopy allowed us to identify the presence of circular structures on the Fe$_3$O$_4$/GaN surface with diameters between 400 to 600 nm. Utilizing transmission electron microscopy and EDS we confirmed that the Fe$_3$O$_4$ deposition formed particles with a “shrub” shape, not a thin film. The results of this work represent another step towards the efficient generation of H$_2$ using nitride-based photocatalysts. We demonstrated that Fe$_3$O$_4$ improves the photocatalytic energy conversion efficiency and prevents the photocorrosion of GaN thin film structures when they are used as photocathodes in alkaline solutions. Thus, Fe$_3$O$_4$ can be added to the list of GaN photocatalysts, which expands the technological applications possibilities of nitride-based semiconductors.

11:45 AM ES11.06.06 Energy Band Alignment and Photonic Design to Enable Photoelectrochemical Water Splitting with >19% Efficiency Wen-Hui Cheng, Matthias H. Richter, Matthias M. May, Jens Ohmann, David Lackner, Frank Dimroth, Thomas Hannappel, Harry Atwater and Hans-Joachim Lewerenz, California Institute of Technology, Pasadena, California, United States; Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany; Department of Physics, Technical University Ilmenau, Ilmenau, Germany.

In photoelectrochemical (PEC) systems, realization of near-limiting photocurrent densities at the thermodynamic potential for water splitting demands careful design of the optical and electronic properties of the surfaces films exposed to the electrolyte. We report unassisted water splitting in a photocathode device utilizing tandem heterojunction III-V semiconductor photocathodes with absorber bandgaps of 1.78 and 1.26 eV. An initial solar-to-hydrogen efficiency of 19.3 % was obtained in acid electrolytes and an efficiency of 18.5 % was achieved at neutral pH conditions under simulated sunlight. Our device approaches 85% of the theoretical limit of realistic water splitting for the light absorber materials. The PEC characterization of the photoelectrode was performed using electron microscopy and energy-dispersive X-ray spectroscopy (EDS).

The thin film GaN homostructure was grown on a c-plane patterned sapphire substrate by metalorganic vapor phase epitaxy and consisted of (top to bottom) unintentionally doped (undoped)-GaN (100 nm)/n-GaN (Si-doped, n=3x10$^{18}$ cm$^{-3}$), 3 µm)/GaN (2 µm). The Fe$_3$O$_4$ cocatalyst was deposited through the spin coating of a metalorganic decomposition solution containing 3 wt% of Fe$_3$O$_4$. The PEC characterization of the photoelectrode was performed using a Pt wire as a cathode, with both electrodes immersed in 1 M NaOH solution and without applying any external electrical bias between the electrodes. The gas volume generated at the cathode and the photocurrent between the electrodes were recorded during the PEC characterization. The gas was characterized using gas chromatography to verify its H$_2$ content.

The observations performed through scanning electron microscopy allowed us to identify the presence of circular structures on the Fe$_3$O$_4$/GaN surface with diameters between 400 to 600 nm. Utilizing transmission electron microscopy and EDS we confirmed that the Fe$_3$O$_4$ deposition formed particles with a “shrub” shape, not a thin film. The results of this work represent another step towards the efficient generation of H$_2$ using nitride-based photocatalysts. We demonstrated that Fe$_3$O$_4$ improves the photocatalytic energy conversion efficiency and prevents the photocorrosion of GaN thin film structures when they are used as photocathodes in alkaline solutions. Thus, Fe$_3$O$_4$ can be added to the list of GaN photocatalysts, which expands the technological applications possibilities of nitride-based semiconductors.


SESSION ES11.07: PEC Benchmarking and Protocols Session Chairs: Todd Deutsch and Chengxiang Xiang Wednesday Afternoon, April 24, 2019 PCC North, 100 Level, Room 121 C
Direct photoelectrochemical (PEC) hydrogen production aims to provide a clean and cost-effective solar fuel. Solar-to-hydrogen (STH) conversion efficiency is central to evaluating and comparing research results, and it largely establishes the prospect for successfully introducing commercial solar water-splitting systems. Present measurement practices do not follow well-defined standards, and common methods potentially impact research results and their implications. We demonstrate underestimated influence factors and experimental strategies for improved accuracy [1].

Our focus is tandem devices that have the prospect for greater STH efficiency [2], but increased complexity that requires more careful consideration of characterization practices. We perform measurements on an advanced version of the classical GaP/GaAs design [3] while considering (i) calibration and adjustment of the illumination light-source; (ii) confirmation of the consistency of results by incident photon-to-current efficiency (IPCE); and (iii) definition and confinement of the active area of the device.

We propose applying the following standards for future PEC performance reporting: (i) traceable disclosure of the illumination-source configuration (lamp, filters, optics, PEC configuration) and/or its measured spectral distribution; (ii) thorough device-area definition including confinement of the illumination area and avoidance of indirect light paths; (iii) complementary IPCE confirmation of the solar-generation potential; and (iv) proper consideration of faradaic efficiency. We will also give a brief overview of the PEC measurements and capabilities available at NREL to support academic and industry research.


1:45 PM ES11.07.02

Measurements of photoelectrode durability in three-electrode (half-cell) configurations are typically not representative of the results obtained for nominally the same electrodes/materials when tested in a two-electrode (full-cell) configuration. While full-cell measurements are the best proxy to predict performance in a deployed photoelectrochemical water-splitting system, there are few materials that can drive both the water reduction and oxidation half-reactions. Component-level or half-cell testing is the only option for materials unable to perform unassisted water splitting. During this talk the results of multiple durability tests, some with and some without a reference electrode, will be used to evaluate key differences between the two types of testing in an effort to elucidate what leads to the incoherency between half- and full-cell measurements. It is anticipated that with this understanding, the photoelectrochemical water-splitting community can begin to move towards an accepted protocol for long-term durability testing that will have more predictive relevance to realistic device configurations.

2:00 PM ES11.07.03
Operando Synchrotron Characterization of Electrochemical Interfaces Walter Drisdell1, Alan Landers2 and Maryam Farmand1; Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Stanford University, Stanford, California, United States.

Electrochemical interfaces are central to water splitting technologies. Knowledge of the chemical mechanisms occurring at these interfaces is invaluable for materials discovery efforts, guiding synthesis for improved catalytic performance or resistance to corrosion. But accurately characterizing these complex buried interfaces under operating conditions is a significant challenge. The high penetration depth and elemental selectivity of synchrotron X-ray methods are ideal for accessing electrochemical interfaces without significantly limiting the chemistry. In this talk I provide an overview of strategies for operando synchrotron characterization of electrochemical interfaces, covering established techniques as well as new capabilities. These include X-ray absorption spectroscopy (XAS), ambient pressure X-ray photoelectron spectroscopy (AP-XPS), and a recently developed system for grazing incidence XAS and X-ray diffraction (XRD) to probe catalyst surfaces under high current conditions. I include examples of these methods applied to water splitting catalysis as part of the Joint Center for Artificial Photosynthesis (JCAP), and discuss potential applications for future studies as well as areas where further capability development is still needed.

2:15 PM ES11.07.04
Anodic Stripping Voltammetry for Detection of Catalyst Corrosion In Situ at Intermediate Current Densities Burton H. Simpson and Chengxiang Xiang; California Institute of Technology, Pasadena, California, United States.

Degradation of catalysts and light absorbers during photoelectrochemical (PEC) water splitting is becoming a critical limitation of PEC devices as efficiencies improve. Inductively coupled plasma mass spectrometry (ICP-MS) is currently the gold standard for detection of corrosion products in such systems, but limits throughput and offers little mechanistic information due to its high sampling time. Here, we demonstrate the use of in situ anodic stripping voltammetry using mercury ultramicroelectrode to detect corrosion products of transition metal catalysts for water splitting. Mercury ultramicroelectrodes can be easily fabricated in any electrochemistry lab and offer faster sampling rates than ICP-MS. Finally, we demonstrate that the improved temporal resolution enables rapid testing of corrosion rates at a range of intermediate current densities applicable to solar driven water splitting.

2:30 PM BREAK

SESSION ES11.08/ES12.06: Joint Session: Water-Splitting Technology Directions
Session Chairs: Katherine Ayers and Ellen Stechel
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 121 C

3:30 PM *ES11.08.01/ES12.06.01
HydroGEN Overview, Projects and the AWSM Node Capabilities (Huyen N. Dinh; Katie Randolph; David Peterson; Adam Weber; Anthony H. McDaniel; Tadashi Ogitsu; Richard Boardman; Donald L. Anton and Eric L. Miller; 1National Renewable Energy Lab, Lakewood, Colorado, United States; 2Fuel Cell Technologies Office, U.S. Department of Energy-EERE, Golden, Colorado, United States; 3Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4SANDIA National Laboratories, Livermore, California, United States; 5Lawrence Livermore National Laboratory, Livermore, California, United States; 6Idaho National Laboratory, Idaho Falls, Idaho, United States; 7Savannah River National Laboratory, Aiken, South Carolina, United States.

HydroGEN (https://www.h2awsm.org/) EMN is a six-lab consortium, led by the National Renewable Energy Laboratory (NREL). It currently comprises six core national laboratories: NREL, SANDIA National Laboratory (SNL), Lawrence Berkeley National Laboratory (LBNL), Idaho National Laboratory (INL), Lawrence Livermore National Laboratory (LLNL), and Savannah River National Laboratory (SRNL). HydroGEN aims to accelerate the discovery and development advanced water splitting materials (AWSM) for sustainable, large-scale hydrogen production, in order to more effectively enable the widespread commercialization of hydrogen and fuel cell technologies. With the rollouts of fuel cell electric vehicles (FCEVs) by major automotive manufacturers underway, enabling AWS technologies for the widespread production of affordable, sustainable hydrogen becomes increasingly important.
The HydroGEN Consortium offers an extensive collection of materials research capabilities for addressing R&D challenges in efficiency, durability and cost. Leveraging the HydroGEN Consortium’s staff of leading technical experts and broad collection of resource capabilities is expected to advance the maturity and technology readiness levels in all the advanced water splitting technologies, including advanced electrolysis (low and high temperature), photoelectrochemical (PEC) and solar thermochemical (STCH) routes. Currently, there are 20 HydroGEN seedling projects, and one project focused on benchmarking advanced water splitting technologies. These 21 new projects utilized over 40 unique capabilities across the six HydroGEN core labs, from computational modeling to material synthesis to advanced characterization. HydroGEN is indeed a national innovation ecosystem that comprises 11 national labs, 7 companies, and 30 universities. This presentation will provide an overview of the HydroGEN EMN consortium and highlight some advanced water electrolysis and PEC projects as well as a few unique HydroGEN capability nodes that the community can leverage.

4:00 PM *ES11.08.02/ES12.06.02
European Efforts to Accelerate the Market Introduction of Renewable Hydrogen Production Martin Roeb1 and Christian Sattler1, 2, 3
1 Institute of Solar Research, German Aerospace Center (DLR), Koeln, Germany; 2 Faculty of Mechanical Science and Engineering, Institute of Power Engineering, Professorship of Solar Fuel Production, TU Dresden, Dresden, Germany.

Converting solar energy efficiently into hydrogen is a key element to develop a sustainable and affordable hydrogen economy. The presentation will give an insight in how concentrated solar radiation can be coupled into hydrogen production processes. It will discuss the benefits and challenges of using the sunlight directly instead of converting it into other energy vectors.

The main focus will be on technologies with the perspective of large scale production at very high temperatures. Therefore solar tower systems for such production processes will be presented. Also the different components like concentrator, receiver, and reactor of the solar production plants will be described, possible locations will be discussed, and synergies with other R&D efforts on using high temperature heat will be shown. Hybrid solutions e.g. from the sulfur industry will demonstrate how concentrated solar radiation can contribute even today to actual industrial business models.

As many of the addressed processes have to be operated continuously high temperature heat storage will also be introduced. Especially thermochemical heat storage has the potential for being the ideal technology for heat storage in high temperature production processes.

The European Union is supporting the development in its research framework programs since the 1980s. However until 2002 only a few projects were carried out. Since then a continuous improvement took place which was accelerated by the implementation of the European Fuel Cell and Hydrogen Joint Undertaking in 2008. This private-public partnership lead by industry is in charge to bring technologies faster into the market than research programs lead by the European Commission would. The presentation will give an overview of the actions carried out so far and the perspective of the European efforts.

4:30 PM *ES11.08.03/ES12.06.03
Benchmarking Water-Splitting Materials at the Intersection of Electrocatalysis and Photoelectrochemistry Tobias Kistler1, Shaun Alia2, Peter Agbo1, Adam Weber3 and Nemanja Danilovic4; 1 Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2 National Renewable Energy Laboratory, Golden, Colorado, United States.

Widespread adoption of inexpensive renewable-electricity sources brings with it many exciting challenges and opportunities, the most significant being an overabundance of low-cost electricity from renewables as well as cheap photovoltaics. Thus, there is an opportunity to use virtually free electrons and photovoltaics to produce fuels and chemicals using electrochemical and photoelectrochemical devices, respectively with water as a reactant. Electrochemical hydrogen production using water electrolysis is a commercial technology, barriers remain in terms of cost and efficiency improvements for its widespread adoption; while alternative water-splitting technologies that have the long-term potential to produce inexpensive hydrogen include photoelectrochemical (PEC) approaches, are still in their infancy. In either case materials development, interface development and cell design are critical in advancing the efficiency and cost of water splitting devices. Benchmarking protocols help to identify promising materials, facilitate translation of materials from one technology readiness level to another, and can provide clear technology crosscutting opportunities. This talk will cover benchmarking activities performed within the HydroGEN Energy Materials Network on: low temperature electrolysis (LTE) electrocatalysts, development of benchmarking cells for photoelectrochemical (PEC) water splitting devices, and crosscutting opportunities between LTE and PEC with respect to the hydrogen evolution and oxygen evolution catalysts activity and durability.

SESSION ES11.09: Poster Session II: Low Temperature Water Splitting via Electrochemistry and Photoelectrochemistry
Session Chairs: Katherine Ayers and Changfeng Yan
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES11.09.01
HydroGEN Supernode—Linking Low Temperature Electrolysis (LTE)/Hybrid Materials to Electrode Properties to Performance Guido Bender1, Shaun Alia1, Michael Ulsh1, Scott Mauger1, Bryan Pivovar1, Huyen N. Din1, Adam Weber3, Nemanja Danilovic2, Ahmet Kusoglu2 and Hector Colon-Mercado2; 1 National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2 Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3 Savannah River National Laboratory, Aiken, South Carolina, United States.

The energy materials network HydroGEN consists of six laboratories that have core capabilities related to hydrogen generation in four technology areas: Photoelectrochemical (PEC), Solar Thermochemical (STCH), High- and Low-Temperature Electrolysis (HTE & LTE). The core capabilities are described as nodes and are available to support projects selected by means of a competitive process through personnel, equipment, expertise, capability, materials, and data exchange and sharing platforms. Starting in the current funding period supernodes were created that combine the unique abilities of the HydroGEN nodes to perform relevant and ground-breaking research outside of the funded projects.

To date, materials advances are required to improve the cost, performance, and durability of LTE and hybrid electrolysis devices. Most materials advances are screened through ex-situ testing protocols due to ease of measurement and throughput. However, properties measured ex-situ are not always relevant for device operation and can be influenced by a number of factors, including synthesis/processing parameters and operating conditions of the individual tests. The optimized integration of novel materials, and the verification that ex-situ results have merit for operating systems is an important detail for accelerating research and development in the electrolysis space.

Savannah River National Laboratory (SRNL), Lawrence Berkeley National Laboratory (LBNL) and National Renewable Energy Laboratory (NREL) have joined several nodes together to probe the connection between materials, electrode composition and processing, and device performance for low temperature electrolysis (LTE)/hybrid electrolysis. This supernode combines/integrates nodes that focus on ex-situ materials characterization, electrode processing, in-situ device characterization, and modeling, so that ex-situ characterization approaches can be validated for their applicability to device performance and durability.

Initial results of the supernode will be presented on typical LTE materials sets that are supposed withstand for example high oxidation potential and high differential pressure. Results may give insights into mass transport challenges and resistivity losses. The presented work is intended to lead up to linking the inherent properties of materials and their composition and processing to observed device performance and durability. These efforts directly support LTE efforts and the low temperature aspects of the combined hybrid cycle.

ES11.09.02
Electrochemical Activity and Adsorbate Effects During Hydrogen Evolution Reactions on Ni/Au Overlayers Calum A. Shelden, Andrew Siwabessy and Hadi Tavassol; Chemistry and Biochemistry, California State University, Long Beach, Long Beach, California, United States.

We report on the electrochemical activity and surface properties of Ni/Au overlayers during the hydrogen evolution reaction. Ni/Au overlayers were prepared using chronopotentiometric deposition of well-defined Ni thin films on Au (111) surfaces from dilute NiSO₄ solutions in 0.1 M H₂SO₄. Using this method, we prepared Ni overlayers with varying thicknesses from 10 nm to 500 nm on Au (111) substrates. X-ray diffraction and scanning electron microscopy analysis of films is used for characterizing the
deposited Ni films. Our electrochemical analysis of these films exhibit that the overpotential required for hydrogen evolution decreases as the thickness of the Ni overlayer increases from ca. 10 nm to 100 nm. Thicker Ni overlayers exhibit higher overpotentials (as high as ca. 150 mV). Interestingly, thicknesses greater than 50nm show additional reductive features in the ca. -50 mV to 400 mV (vs. RHE) potential range. Ni overlayers also suppress features associated with sulfate interactions with Au surfaces. Such high activity of Ni/Au overlayers are significant, especially considering the stability region of Ni in acidic media. We will present results from surface enhanced Raman spectroscopy analysis of these surfaces in electrochemical solutions, and optical in-situ surface stress measurements to probe adsorbate effects during hydrogen evolution reactions on Ni/Au overlayers.

**ES11.09.04**

**Advancements in High Temperature Proton-Conducting Electrolyzer Materials**

Dong Ding

Idaho National Laboratory, Idaho Falls, Idaho, United States.

Advanced in super-proton conducting materials are being made under the DOE HydroGEN Energy Material Network. The desired goal is to reduce the operating temperature of high temperature steam electrolysis to around 600°C or less to reduce degradation and fouling of the electrode/electrolyte, interconnections, and associated stack containment and gas handling materials. Four projects funded under the DOE HydroGEN program are focusing on various aspects of materials development and testing. Methods for fabricating these materials are being developed and tested by various experimental capabilities (nodes) within the designated HydroGEN core labs. Initial testing is focusing on the performance of these materials.

**ES11.09.03**

**HydroGEN PEC Supernode—Emergent Degradation Mechanisms with Integration and Scale up of PEC Devices**

James L. Young

Nemanja Danilovic

Myles Steiner

Francesca Maria Toma

Genevieve Saur

Judith C. Vidal

Hanna Brunig

Daniel J. Friedman

Adam Weber

Todd G. Deutsch

National Renewable Energy Laboratory, Golden, Colorado, United States;

Lawrence Berkeley National Laboratory, Berkeley, California, United States.

In this talk we will give an overview of the HydroGEN photoelectrochemical (PEC) water-splitting Supernode and present recent progress. This Supernode project is collaboration of nine PEC capability nodes that are part of the HydroGEN Advanced Water Splitting Materials consortium. These nodes are bundled to collaboratively develop an understanding of integration issues and degradation mechanisms that emerge as PEC devices move from the current research scale, typically 1 cm², to 10s of cm² and greater that are necessary to consider a PEC module or panel. Larger devices are expected to introduce new component integration challenges and pathways for degradation that this PEC Supernode project seeks to identify while suggesting routes to take that should maximize success in the upscaling process.

The PEC Supernode project is an alliance of synthesis, characterization, and modeling nodes housed at the National Renewable Energy Laboratory and Lawrence Berkeley National Laboratory whose tasks include: 1) Photoreactor chassis fabrication and baselining, 2) development, fabrication, and testing of larger area PEC devices based on tandem III-V absorbers, 3) development of in-situ morphology and corrosion analysis techniques and characterization, and 4) analysis of durability mechanisms and impacts using life cycle analysis and techno-economic analysis. We will also describe a new photoreactor chassis that has been designed to facilitate indoor and on-sun efficiency and durability benchmarking measurements. The design has been validated in a preliminary set of multi-institution round robin testing toward understanding and harmonizing measuring conditions and protocol, which will be elaborated upon here.

**ES11.09.05**

**Chemomechanical Effects During the Hydrogen Evolution Reaction on Pt-Cu Surfaces**

Andrew Siwabessy

Andrea Nelson and Hadi Tavassoli; California State University, Long Beach, Long Beach, California, United States.

We report on the surface and subsurface hydrogen evolution reactions on well-defined platinum/silver surfaces in electrochemical environments during the hydrogen evolution reaction (HER). We are particularly focused on the Pt-Cu binary system. Well-defined surfaces of Pt and Cu/PT are prepared using thermal evaporation and electrodeposition, respectively. An optical laser method is used to perform in-situ surface stress measurements to track early stages of catalyst activation through adsorbate-induced effects. Surface stress changes on Pt surfaces show a distinctive compressive feature as hydrogen is adsorbed onto the Pt surfaces. The magnitude of this compressive feature decreases with increasing scan rates, which implies fast surface activation of hydrogen. Interestingly, the magnitude and potential dependence of the hydrogen-specific surface stress changes do not change as the solution pH changes (between pH = 1, 7 and 14). However, surface stresses change significantly in the presence of H₂ gas.

Additionally, hydrogen-specific stress changes are completely suppressed in the presence of ultra-thin copper overlayers. Our analysis shows that the adsorption of active species, i.e. H⁺ at the catalyst's active sites, causes structural changes and clearly demonstrates that the early stages of adsorbate formation could describe electrocatalysis and surface/subsurface structural effects. We will further discuss surface tuning of the Cu-Pt system for improved hydrogen evolution reactivity using insight from our in-situ analysis.

**ES11.09.06**

**Chalcopyrite Alloy Materials for PEC H₂ Production—Development of Theoretical Synthesis Support System for HydroGEN**

Joel B. Varley

Abhishek Sharan

Anderson Janotti

Nicolas Gaillard

Alexander DeAngelis

Tadashi Ogitsu

Lawrence Livermore National Lab, Livermore, California, United States;

University of Delaware, Newark, Delaware, United States;

University of Hawaii, Honolulu, Hawaii, United States.

Chalcopyrite alloy materials class is an attractive candidate for photovoltaic (PV) and photoelectrochemical (PEC) devices due to its high bandgap tunability and presence of low cost synthesis pathways. However, these advantages are also known to be associated with challenges in the materials synthesis as well as the device assembly processes. For example, certain chalcopyrite alloys exhibit strong tendency of developing secondary phase(s) during its synthesis, which affects on the device performance in unpredictable manner: it could be beneficial or detrimental depending on the alloy composition and the synthesis condition.

In this presentation, we first review the issue of secondary phases, such as ordered vacancy compound (OVC), reported in literature as well as our recent findings on sulfur containing chalcopyrite materials synthesis, where sulfur was incorporated in order to achieve an optimal band alignment for a PEC H₂ production device. The electronic property of OVC interacts with both the photoabsorber (chalcopyrite) and the buffer, where the defect properties of these materials play crucial roles in the functionality of hetero junction (ex. charge carrier separation efficiency, open circuit voltage). In order to find the synthesis routes that would minimize the detrimental effect of OVC formation and its intrinsic defects to the performance of complex hetero-junction (absorber-OVC-buffer), we have been developing thermodynamic alloy phase diagram of candidate photoabsorber materials that includes OVCs as well as the corresponding defect property database. We will discuss how these data may be used to predict the device performance (ex. open circuit voltage) behavior, which in turn, may be used to strategize the PEC/PV device development.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory Under Contract DE-AC52-07NA27344, and is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.

**ES11.09.07**

**Photoelectrochemical and Low Temperature Water Splitting Materials Research at Lawrence Livermore National Laboratory Under HydroGEN Consortium**

Tadashi Ogitsu

Brandon C. Wood, Tuan Anh Pham, Joel B. Varley, Jonathan Lee, Monika Biener, Chris Orme and Yong Han; Lawrence Livermore National Lab, Livermore, California, United States.

The HydroGEN consortium brings together unique DOE National Laboratory experts and tools (nodes) with researchers developing advanced water splitting materials in a variety of technologies: Low and High -Temperature Electrolysis (LTE/HTE), Photoelectrochemical (PEC) and Solar-Thermochemical (STCH) Water Splitting. Lawrence Livermore National Laboratory is a HydroGEN partner lab and has participated in 4 projects since 2018. This poster will highlight:

- Livermore Lab capabilities and expertise available to researchers in LTE, HTE, PEC and STCH fields
- Our collaborative work performed with our partners in LTE and PEC in FY18.
- Tackling big scale problems in PEC, LTE, HTE and STCH through multi-node, multi-institution projects "supernodes"
- Come and ask questions as to how we could help your water splitting research

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, and is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office.
A Demonstration of Supported Iridium Oxohydroxide as the Low Noble Loading Anode in PEM Water Electrolyser


The reduction of noble loading in PEM water electrolyser is still a big challenge, especially in the anode. Using the supported catalysts can reduce the amount of Iridium in anode significantly, some reports have achieved very low loading of iridium (about 0.1mg/cm²) in anode catalyst layer. Recently, Iridium oxohydroxide has been reported as a highly active catalyst for oxygen evolution, and it has also been supported on ATO to form a supported catalyst, however, this catalyst has not been demonstrated in PEM water electrolyser. To show the advantage of such supported catalyst, Iridium oxohydroxide was supported on titanium nanosphere in this work, and membrane electrode assemblies were prepared to achieve the low noble loading in PEM water electrolyser.

Titanium nanosphere with the diameter range form 60-200 nm was chosen as the support, the Iridium oxohydroxide was supported on it by hydrolysis method reported by Strasser’s group. The mass activity of Ir was range from 800-1600 mA/g (g=0.37V), which depends on the loading percentage on the support. We found that lower loading of Ir on support can achieve higher mass activity, and this may be due to the higher dispersion of IrOx on Ti nanosphere. The MEA with only 0.24mg/cm² Ir loading achieved 1.735V cell voltage with thicker Nafion 117 membrane, and the voltage can be reduced further by using thinner membrane. We also found that higher loading percentage of catalyst is better for achieving higher performance of water electrolyser with the same Ir loading in MEA. This must be because, on one hand, the higher loading percentage of Ir in catalysts can form a thinner catalyst layer when preparing MEA, and it will facilitate the mass transport of water and oxygen. On the other hand, larger ECSA will benefit from higher loading percentage of Ir in catalysts, because more active sites can contact with membrane.

In summary, our studies exhibited the supported Iridium oxohydroxide is a good catalyst for reducing the Ir loading in PEM water electrolyser. The Ir loading can be reduced to 0.24mg/cm² with no significant performance loss for PEM water electrolyser, and the further work will focus on performance optimizing and stability of PEM water electrolyser with such new MEAs.

ES11.09.10

Alkaline Water Electrolysis at 20 A cm⁻² with a Microfibrous, Flow-Through Electrolyzer

Feichen Yang, Myung Jun Kim and Benjamin Wiley; Chemistry, Duke University, Durham, North Carolina, United States.

Improving both the efficiency and productivity of water electrolysis is necessary for making the electrochemical generation of hydrogen economically competitive. The efficiency depends on the surface area and catalytic activity of the electrode, whereas the productivity depends on the ease with which gas can be removed from the electrode surface. Flow-through electrodes are widely used to improve the efficiency and productivity of electrochemical processes, but studies of their use in alkaline water electrolysis are relatively rare. We hypothesized that the use of a flow-through electrode could enhance the rate of bubble removal from the electrode surface, thereby improving productivity, but it was not clear what length scale of the electrode would maximize the surface area available for electrolysis without hindering bubble removal. To determine how the efficiency and productivity of the flow-through electrode depends on the electrode length scale, we compared the performance of the oxygen evolution reaction with flow-through electrodes consisting of a Ni foam, Ni microfibers (Ni MFs, d = 1.2 mm), and Ni-coated Cu nanowires (NiCu NWs, d = 350 nm). Although the turnover frequency (TOF) for the Ni foam was 2.4 times higher than the Ni MF electrode and 42 times higher than the NiCu NW electrode, its surface area was more than 90 times lower than the other electrodes, resulting in the lowest overall current density. Although the NiCu NW electrode had a higher surface area than the Ni MF electrode, it had a lower overall current density because of its low TOF. We attribute the higher performance of the Ni MF electrode to the fact that the mean pore size of the Ni MF electrode (5-10 mm) is on the order of the mean bubble size (20 mm) that was measured by examining the bubbles generated from a mesh electrode under an optical microscope. The performance of the Ni MF electrode was further improved by coating it with a Ni-Fe layered double hydroxide (LDH) catalyst, resulting in an OER overpotential of 247 mV at 0.1 A cm⁻² and a Tafel slope of 26 mV dec⁻¹. These values are among the lowest reported for Ni-Fe LDH catalysts. The LDH-coated Ni MF anode was paired with a cathode coated with a Ni-Mo alloy to measure the overall productivity for water splitting. The maximum current density for water splitting was 20 A cm⁻² at 3.9 V in 30% KOH, which is 20 times greater than the highest current densities previously reported for alkaline water electrolysis. This current density and voltage could be sustained for at least 8 hours with no signs of degradation. This high current density was attributed to the ability of the flowing fluid to promote bubble removal and keep the hot electrode surface from boiling water. This work demonstrates that flow-through microfibrous electrodes can improve the efficiency and productivity of alkaline water electrolysis.

ES11.09.11

Hierarchical Porous Ni₃CoₓSnSe₄ Nanostructures on Nickel Foam as High Efficient Water Oxidation Catalyst Synthesized Through a Facile Route

Jianping Xin; State Key Laboratory of Crystal Materials, Shandong University, Jinan, China.

Electrochemical water splitting is considered as one of the most robust way to generate hydrogen gas as an alternative to traditional fossil fuels to relieve the energy crisis and environmental changes. Compared with hydrogen evolution reaction, oxygen evolution reaction involves four-electron redox processes, and generally this sluggish process determines the rate of water splitting and significantly hinders the improvement of the overall efficiency. To address this issue, a great deal of effort has been devoted to develop high performance OER electrocatalysts to facilitate the reaction kinetics. To date, noble metal based catalysts such as IrO₂ and RuO₂ are still the benchmark electrocatalysts for OER, but their scarcity and high cost immensely limit their large-scale and widespread deployment. Therefore, it is imperative to develop noble-metal-free electrocatalysts with high activity and good durability. In recent years, transition metal compounds as a class of candidates ranging from oxides, hydroxides, phosphates, nitrides to chalcogenides, have attracted significant attention due to their unique electronic and relatively high efficiency for OER. Nevertheless, the catalytic activity of the existing catalysts still falls short of expectations. For this reason, designing and synthesizing new materials is a promising way to realize the massive boost of the OER catalytic efficiency. Herein, we report the synthesis of nickel-cobalt selenite (Ni₃CoₓSnSe₄) networks on a nickel foam with promising electrocatalytic performance through a facile electrodeposition method. The networked structure built with interconnected nanosheets along with the three-dimensional backbone of nickel foam is able to provide large surface area for the reaction to take place and simultaneously offer the connected channels for charge carriers to pass through, consequently, realizing the enhancement of oxygen evolution reaction (OER) electrocatalytic activity. Importantly, the multilevel channel structure achieves vast spaces to buffer the volume change during repeated redox reactions and offers favorable channels for gas release, leading to the good electrochemical stability. The best sample with optimized composition shows superior catalytic activity with high current density of 243.6 mA cm⁻² at the overpotential of 500 mV and excellent stability.

ES11.09.12

Effect of Boron Chain in Vanadium Boride Hydrogen Evolution Reaction Electrocatatysts

Eusoom Lee and Boniface Fokwa; Chemistry, University of California, Riverside, Riverside, California, United States.

In order to generate hydrogen, which is promising fuel in the future, electrochemical water splitting through hydrogen evolution reaction (HER) have taken center stage. Although, existing catalysts for HER such as platinum group metals have been considered the best catalyst, they have problems with high cost and scarcity. Recently, transition metal boride (TMBS) has been considered potential HER electrocatalysts and various covalent networks of boron in the crystal structure have meaningful relation with electrocatalytic activity for HER. In this work, we synthesize vanadium borides which have different boron chains by arc melting; VB (zig-zag chains), V₄Bₙ (double chains), and VBₓ (flat hexagonal chains). The open circuit voltage of a conventional H₂O₂ fuel cell is limited to ~1.23 V under atmospheric pressure, which limits the efficiency of the system. Here, we reported a dual-electrolyte microfluidic fuel cell system (DEFC), which could stably deliver an open circuit voltage up to 1.76 V at room temperature under atmospheric pressure, and a peak power density of 145 mW/cm², improved by 3 times compared with that in single electrolyte mode. When operated in the reverse mode, the microfluidic cell can be used for water electrolysis, demonstrating a water split voltage of ~0.74 V and a round trip voltage efficiency of 83.5% at a current density of 100 mA/cm². The neutralization energy of the two electrolytes, which could be wasted as heat, can be directly utilized to produce electricity or split water with high efficiency. Given the DEFC’s features of high open-circuit voltage, low water splitting voltage, and room-temperature operation condition, the reported DEFCs technology presents a superior route for high-efficiency energy conversion and storage system that could revolutionize the fields of large-scale energy storage and portable power systems.
network). Electrochemical measurements show that VB$_2$ requires the lower overpotentials (-0.360 V) than that of VB (-0.430 V) and V$_3$B$_5$O$_{11.6}$ (0.416 V) in 0.5 M H$_2$SO$_4$ to achieve a current density of 100 mA/cm$^2$. Besides, the activity of VB$_2$ is remained after 5000 cyclic voltammetry measurements. These results indicate that graphene-like flat boron layers in VB$_2$ give positive effect for increasing HER activity due to its electrical conductivity and Ag$_3$ value close to 0 V.

ES11.09.13
Engineering on Ni-Co-S Bifunctional Electrocatalyst for Water-Splitting Jing Wu, Huijing Guo, Zhao Kang and Yue Zhang; State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology, Beijing, China.

Ni-Co-S is a technologically important electrode material that has recently achieved remarkable performance in catalysis. Herein, Ni$_{1-x}$Co$_x$S$_2$ bifunctional catalysts with tunable stoichiometry was synthesized on Ni foams. The electronic structure engineering contributed to the significantly elevated electrocatalytic performance. As a result, overpotentials $\eta_0$ of 97 mV (vs.RHE) for hydrogen evolution reaction (HER) and 285 mV for oxygen evolution reaction (OER) in 1M KOH solution. At the same time, we study the electrocatalytic properties of the NiCo$_2$S$_4$ by using density functional theory, the Gibbs free energy changes of different active sites shows the Co top site of the (011) surface is the most active site. The excellent catalytic activities are attributed to the optimal electronic structure of catalyst surface, we found the different atomic ratios between Ni and Co have significant impact on the electronic structure by calculating the electron density difference of Ni$_{1-x}$Co$_x$S$_2$.

ES11.09.14
Leveraging Plasmas for Electrochemical Fuel Production—Synthesizing Novel Low-PGM OER Catalysts and Enhancing the Rate of Electrochemical Ammonia Production Joshua M. Spurgeon, Sudesh M. Kumari and Sahar M. Pishgar; Conn Center for Renewable Energy Research, University of Louisville, Louisville, Kentucky, United States.

Plasmas have a number of unique properties which researchers may be able to leverage to enhance desired electrocatalyst material properties and steer electrochemical reaction performance. Two examples of the recent application of plasmas for advancements in electrochemical fuel production are presented. In the first, the nonequilibrium reaction environment of an air plasma enabled the synthesis of homogeneous phases of metastable mixtures of a mixed W$_x$Ir$_{1-x}$O$_2$ alloy. For a low-platinum-group-metal (PGM) composition of only 1% Ir, plasma-synthesized W$_9$Ir$_{10}$O$_{29}$ was observed to be an acid-stable oxygen evolution reaction (OER) catalyst of competitive overpotential. Moreover, the plasma-synthesized alloy was observed to have an OER overpotential ~ 570 mV less than that of a thermally oxidized alloy of the same composition. In the second example of a plasma enhancement, a nitrogen plasma was coupled into the cathode of a proton exchange membrane electrolyzer to provide energetically activated N$_2$ species to the electrocatalyst surface and demonstrate a proof-of-concept synergistic enhancement in the rate of ammonia production. At an applied bias of ~3.5 V across the electrolyzer, plasma-assisted operation was observed to produce 47% more ammonia than the combination of plasma-without-bias and bias-without-plasma conditions.

ES11.09.15

Due to the extreme conditions encountered during typical use; solar thermochemical (STCH) water splitting materials that do not begin in a low energy state will evolve during cycling. Evolution during cycling may take many forms, including Oswald ripening of grains or slow conversion of impurity phases, all of which will have some effect on the performance of the material during cycling. Thus, creating phase pure materials with stable grain sizes is of utmost importance to evaluating STCH materials. We report on the methods of designing high quality STCH materials from the modeling stage onwards, the synthesis of phase-pure and pre-ripened materials, and characterization used to determine the stability of the material over many cycles.

ES11.09.16
Developing an Atomic Understanding of the Layered Perovskite Ba$_{2}$CeMn$_{2}$O$_{6}$ and Its Polytypes for Thermochemical Water Splitting—A HydroGEN Supernode Anthony H. McDaniel, Andrea Ambrosini, Eric Coker, Joshua Sugar, Robert T. Bell, David S. Ginley, Stephan Lany, Philip Parilla, Tadashi Ogitsu, Sabrina Wan and Brandon Wood; Sandia National Laboratories, Livermore, California, United States; Sandia National Laboratories, Albuquerque, New Mexico, United States; National Renewable Energy Laboratory, Golden, Colorado, United States; Lawrence Livermore National Laboratory, Livermore, California, United States.

Next generation perovskite-oxide based materials for thermochemical water splitting (aka STCH) are key to developing a massively scalable technology that efficiently converts solar energy to hydrogen. The challenge is to design optimal perovskites that achieve DOE performance targets, such as high efficiency operation at low thermal reduction temperature. Current research is mired in a heuristic approach to probing the enormous array of possible material compositions that manifest water splitting activity in perovskites. A comprehensive molecular-level picture of the factors that influence redox cycle behavior is missing. We report on a HydroGEN Advanced Water Splitting Materials (H2AWSM) consortium effort to develop a fundamental understanding of how the unique crystallographic structures induced by the Mn$_x$O$_{y}$ ligand bond found in layered perovskites influences properties critical to favorable material behavior. This is accomplished by examining perovskite electronic structures resulting from redox transitions using advanced spectral microscopies and, in conjunction with atomistic theory, deriving correlations between electronic configurations and thermodynamic properties that manifest water splitting material behavior.

ES11.09.17
Bifunctional Oxygen and Hydrogen Evolution Electrocatalytic Activities of P-Type Delafossite Cu$_2$Mo$_3$O$_7$ Oxides Yuanbing Mao; The University of Texas at Rio Grande Valley, Edinburg, Texas, United States.

Making easy-to-make, cost-efficient, and durable bifunctional electrocatalysts for overall water splitting to produce oxygen and hydrogen is of paramount significance for future renewable energy system but still a challenge. Herein, we explored earth-abundant and non-toxic delafossites with a CuMo$_2$-type general composition, where ‘M’ is trivalent metals of Al, Ga, Cz, Co, Fe, etc. First, we report that nanocrystalline CuGa$_2$O$_4$ hexagons showed enhanced electro-catalytic activity as compared to the sub-micron sized and micron sized particles of CuGa$_2$O$_4$ counterparts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in 0.5 M KOH versus Ag/AgCl. Then, based on a widely used strategy to increase the surface area of functional materials, we synthesized delafossite CuGa$_2$O$_4$ nanoflakes. Their electrochemical (EC) and photoelectrochemical (PEC) performance in 0.5 M KOH electrolyte versus Ag/AgCl along with their stability were studied. The developed electrocatalysts are very efficient to produce H$_2$ cheaper, offers no complications in synthesis of materials and fabrication of electrolyzers, which can greatly enable the realization of clean renewable energy infrastructure.

ES11.09.18

Pacific Northwest National Laboratory’s (PNNL) experience in solid oxide electrolysis cell (SOEC) technology and related high temperature electrochemical devices extends back to 1987 and has been documented in over 150 peer-reviewed technical papers and numerous patents. PNNL’s experimental and modeling experience and capabilities in high temperature electrochemistry encompass all aspects of the technology, from materials development and characterization to design, fabrication, and testing of cells, stacks, and systems. In addition to performing work for the U.S. Department of Energy and other agencies, PNNL has collaborated successfully with a number of industrial developers. PNNL’s high temperature electrochemistry laboratories contain all the materials synthesis, processing, fabrication and testing equipment necessary to develop and test solid oxide electrolyzers, stacks, and complete power systems. The experimental work is being supported by computational modeling at the cell, stack, and system levels. PNNL also hosts a national user facility, the Environmental Molecular Sciences Laboratory, with a large suite of physical and chemical characterization tools.
With the gradual consumption of fossil fuels and rapidly increasing pressures from environmental pollution, it is important and necessary to develop and harvest clean renewable energy in large scales to fulfill the sustainable development in economy and society. Hydrogen generated from electrochemical water splitting can not only replace fossil fuels as a clean and efficient energy carrier, but also realize large-scale conversion and storage of sustainable energy-produced electricity. Generally, electrocatalytic water splitting consists of two half reactions, namely hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), while an additional potential is required for the implementation because of the limitation in slow cathodic and anodic kinetics. Non-noble metal-based electrocatalysts (such as manganese, iron, cobalt, and nickel) are of huge advantages in the low cost and rich abundance as compared with noble metals, but their activity and stability are still not satisfactory for practical applications. In this regard, rational design of the structures and composites of hierarchical electrocatalysts using various strategies are widely explored to aim for reducing the overpotentials for efficient water splitting. Typical methods include controlling the morphology, employing the conductive substrates as supports, regulating the ratios of various constituent components, engineering the defects, doping with the foreign elements, as well as surface coating and decoration in order to enhance the catalytic activity and stability of electrocatalysts. Recently, more attentions are paid on regulating the catalytic activity of catalysts by incorporating with rare earth elements. Because of the stable chemical property and unique electronic structure of rare earth elements, their integration with hierarchical transition metal-based electrocatalysts is developed as a novel method to modify the structure and property of electrocatalysts. In this presentation, cerium as a typical rare earth element, is selected and introduced into the transition metal-based electrocatalysts to improve their HER and OER properties. The role of cerium-based species and their influences on the structures and properties of electrocatalysts are also investigated.

References:

Hydrogen, as an eco-friendly energy resource with the highest energy density, has attracted lots of attention due to the current environmental and energy issues. Electrocatalytic hydrogen production by water splitting can potentially meet the needs for renewable energy storage into clean fuels. The electrode design and fabrication are always the key to lower the reaction overpotential and increase the energy efficiency. Our group use layered double hydroxides-based catalysts as demonstration. By controlling the chemical composition and designing defect structure or single atom site, the intrinsic activity of such catalysts can be largely enhanced.1-6 1-6 Constructing nanoarray structure would help exposing more edge/unsaturated active sites for electrocatalysis.1-6 Non-noble metal alloy nanosheet array was developed by topotactic conversion from layered double hydroxides for bifunctional electrode.1-6 Our strategy opens a new door for the development of water-splitting technologies and energy conversion.

References:
Scientists (WDTS) under the Science Undergraduate Laboratory Internship (SULI) program. This work was also supported in part by Workforce Development & Education at Berkeley Lab.


10:00 AM *SESSION ES11.11: HER Electrocatalysis*

**Synthesis and Microstructural Evolution of Pt Free Highly Efficient MoNi4 Nano Electrocatalyst for Hydrogen Evolution Reaction**

**Pei Kang Shen**

Guangxi University, Nanning, China.

A review concerning our systematical work on water splitting and hydrogen evolution reaction is presented. Various compounds doped with one or more elements catalysts have been synthesized and used for water splitting or hydrogen evolution reaction. Such materials show better or even better than Pt-based precious metal catalysts in performance. It has been realized that the low temperature electrolysis (LTE) produces cost-competitive renewable hydrogen can be directly used in the transportation sector for fuel cell cars.

Some of the effective catalysts for water splitting and hydrogen evolution are presented and the performance will be shown and discussed.

**References:**


11:00 AM *SESSION ES11.11.02*

**Highly Active Electrocatalysts for Efficient Water Splitting and Hydrogen Generation**

**Pei Kang Shen**

Guangxi University, Nanning, China.

A review concerning our systematical work on water splitting and hydrogen evolution reaction is presented. Various compounds doped with one or more elements catalysts have been synthesized and used for water splitting or hydrogen evolution reaction. Such materials show better or even better than Pt-based precious metal catalysts in performance. It has been realized that the low temperature electrolysis (LTE) produces cost-competitive renewable hydrogen can be directly used in the transportation sector for fuel cell cars.

Some of the effective catalysts for water splitting and hydrogen evolution are presented and the performance will be shown and discussed.

**References:**


Molecular hydrogen is the most promising candidate for clean, renewable and economical energy carrier to address the every increasing demand for clean energy. However bottleneck for large scale commercialization of the water electrolyzer is the requirement of costly Pt electrocatalyst. Search for efficient and cheaper alternatives based on Earth abundant elements is limited by the slow kinetics of the Volmer step for adsorption of hydrogen and subsequent Tafel step for generation of molecular hydrogen from recombination of adsorbed H atoms. In a recent work MoNi4 electrocatalyst supported on MoO2 is synthesized from thermal reduction of NiMoO4. Very high efficiency for HER with 0 mV onset over potential tafel slope ~30 mV/decade has been reported which originated from drastically accelerated Volmer and Tafel steps. However detail understanding for microstructural evolution, alloy formation and phase separation during thermal reduction of NiMoO4 along with the role of MoO2 is required for further improvement of the catalyst. In the present work detail Transmission electron microscopic studies including in-situ heating, nanobeam diffraction and STEM-EDS is used for comprehensive understanding of the growth mechanism of the electrocatalyst. Role of each of the co components of the electrocatalyst and their stabilities are evaluated through impedance spectroscopy and array of other electro chemical techniques.
finding suggests that dissolution occurs from distinct surface sites from those that are responsible for O₂ evolution. This understanding corroborates our earlier work, which showed that surface Ir stabilises RuO₂ and surface Ti stabilises MnO₂, without compromising activity. On this basis, we propose there should be ample opportunities for engendering further improvements to the stability of oxygen evolution catalysts under acidic conditions.


2:30 PM ES11.12.03
The Role of Catalyst Metastability in Enhancing the Oxygen Evolution Reaction
Nathalie Vornrütii and Ulrich Aschauer; Chemistry and Biochemistry, Universität Bern, Bern, Switzerland.

While it was shown that metastability can increase a catalyst’s water-oxidation activity (1,2) it is still unclear what the underlying mechanism is. Using density functional theory calculations, we analyze the oxygen evolution reaction (OER) on (001) surfaces of three different materials chosen for their very different electronic properties. To account for the metastability, we study the OER on a large variety of different reaction sites by sampling many defective surface structures. Totally, we compute the OER overpotential on 770 symmetrically inequivalent reaction sites. For all three materials, we find a large range of overpotentials for different reaction sites including also overpotentials at the top of the activity volcano. This implies that the structural variety of reaction sites on dissolving metastable heterogeneous catalysts will, for some sites, lead to overpotentials close to the top of the activity volcano. Under the assumption that reaction sites with low overpotentials will dominate a catalyst's apparent activity, this implies that, independent of the electronic properties of the catalyst, operating a heterogeneous catalyst at the border of its stability region can lead to an increased apparent activity due to the large geometric variety of different reaction sites.


Funding Acknowledgement
Swiss National Science Foundation PP00P2_157615

2:45 PM ES11.12.05
Controlled Electro-Deposition of IrO₂ Nano-Arrays with Different Length on TiO₂ Nanotube Arrays
Zhao-xin Lu, Yan Shi, Chang-qing Guo, Zhi-da Wang, Hong-yi Tan and Changfeng Yan; Hydrogen Production and Utilization Lab, Guangzhou Institute of Energy Conversion, Chinese Academy of Science, Guangzhou, China.

One-dimensional-arrays material possesses high surface area, oriented electron transfer pathway and facile mass transfer pathway, which shows prominent potential for electrocatalyst. IrO₂ nano-arrays (IrO₂ NAs) performs excellent activity in oxygen evolution reaction in electrochemical water splitting. In this work, TiO₂ nanotube arrays (TNTA) with a length of 1500 nm is applied as template to study electrodeposition of IrO₂ on conductive nanotube substrate through cyclic voltammetry (CV). By conducting different scan rate of CV and concentration of Ir precursor in electrodeposition, IrO₂ NAs, nanotubes or hollow nanowires, with different length is obtained, which is determined by the distribution of deposited IrO₂ under different applied conditions. With fixed concentration of Ir precursor, there is a positive-related linear range between scan rate and the length of IrO₂ NAs that is the depth of TNTA where deposited IrO₂ could construct constant layer on the tube wall. A possible mechanism is proposed. As the whole tube wall of TNTA is conductive, the electrodeposition of IrO₂ will take place throughout the tube. Due to the competition of the consuming of Ir precursor by depositing and supplementing through diffusion from bulk electrolyte, concentration gradient of Ir precursor would be gradually formed along the tube and leads to uneven depositing. And this phenomenon would be exacerbated with the prolongation of depositing time. In electrodepositing of CV, each cycle includes the depositing period and non-depositing period in which Ir precursor could be sufficiently diffused throughout the TNTA. And with a slower scan rate of CV the uneven depositing will be more significant. Besides, as the CV depositing goes on, a cover layer of IrO₂ on the top surface of TNTA, which would hinder the diffusion of Ir precursor form the bulk electrolyte to inner zone of TNTA, would be formed as we have reported. As the depositing rate near the mouth of TNTA will be hardly affected by the prolongation of depositing period of each cycle, the formation of cover layer is mainly determined by the total depositing time, while the deposited amount of IrO₂ in the depth of TNTA depends on the cycles of CV. Briefly, the length of obtained IrO₂ NAs is determined by the number of depositing cycles before the cover layer is formed. The deposition with different concentration of Ir precursor and fixed scan rate has been studied, too. With lower concentration, the required numbers to form cover layer increases, and results in longer IrO₂ NAs, which is consistent to our proposed mechanism.

3:00 PM BREAK

SESSION ES11.13: Stack Level Perspective
Session Chair: Peter Strasser
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 121 C

3:30 PM ES11.13.01
Effects of Low Loading and Intermittency on Low Temperature Electrolysis from a Catalyst Perspective
Shaun Aila¹, Shraboni Ghoshal¹, Grace Anderson¹, Mai-Anh Ha¹, Sarah Stariha², Chilan Ngo³, Svitlana Pylypenko³, Rod Borup² and Ross Larsen¹;¹National Renewable Energy Laboratory, Lakewood, Colorado, United States; ²Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ³Colorado School of Mines, Golden, Colorado, United States.

In commercial electrolysis, the cost of electricity input drives the cost of hydrogen production. Electrolysis, therefore, is typically run at high catalyst loading and constant power input over long periods of time. Lowering water-splitting hydrogen production costs to a level comparable to steam methane reforming requires: coupling electrolysis with low-cost power input (wind, solar) to reduce feedstock costs; and minimizing capital cost at lower capacity. [1,2] Part of reducing capital cost includes reducing catalyst loading and while minimal durability loss is seen with thick catalyst layers, losses become more apparent with loading reductions.[3]
Presented efforts include evaluating load-follow operation, start-stop operation, and contaminants, studying relevant mechanisms for loss in half-cell tests and how these losses are observed in single-cell tests. Electrolyzer durability was evaluated at low iridium-anode loading (0.1–0.5 mg cm⁻²) and with different power inputs (potentials, intermittency) to focus on systems aspects needed to significantly reduce hydrogen production costs. Within load-follow operation, iridium loss was driven by dissolution. Although higher potential accelerated single-cell loss, cycling (square/triangle wave) also increased the rate of performance decay since rapidly increasing input resulted in localized potential spikes within the catalyst layer. While start-stop operation accelerates loss through a variety of pathways (dry operation on membrane, pressure cycling on membrane and hydrogen crossover), these efforts focused on the effect of potential excursions on the catalyst. Simulated hard-stops were more detrimental to iridium durability than load-follow, likely due to surface and near-surface reduction increasing dissolution rates. The effect of contaminants was also evaluated based on likely metals added with water input. Contaminant effects in half-cell tests were observed but were relatively small and may have been due to the large amount of free electrolyte and desorption on iridium at high potential. Losses were more significant in single-cells and may have been exacerbated by contaminants blocking within the membrane and plating the cathode.

Several catalyst types have been tested, including metals (metal/hydroxide) and oxides with supports, high surface area, multicomponent, and alloys. These materials have been

studied in half-cells for the activity improvement mechanism and in single-cells to evaluate potential advantages/disadvantages in electrolysis performance and durability. By including different catalyst types, we are looking to establish performance/durability guidelines and perspectives on how catalyst development and system controls factor into low temperature electrolysis at low loading and with intermittency. These tests have significant implications with a shift toward low-cost hydrogen production through electrolysis coupled with renewable power inputs.


4:00 PM  *ES11.13.02  Alkaline Membrane Electrolysis—Challenges and Perspectives Hui Xu; Giner Inc., Newton, Massachusetts, United States.

The utilization of renewable energy has substantially driven more attention into electrolysis technologies. An electrolyzer can utilize “off peak” electricity from solar or wind farms to produce hydrogen or other fuels. These fuels can then be operated in a fuel cell mode to generate electricity when needed or used for other industrial applications. Further, the establishment of H2@scale consortium by DOE has presented unprecedented opportunities for renewable H2. However, current hydrogen production from electrolysis comprises only a small fraction of the global hydrogen market due to the high costs that result from expensive materials even if “free” electricity from renewable energy can be acquired.

Alkaline membrane water electrolysis enables to use non-precious metals (or oxides) as the catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The commercial OER catalyst IrOx for proton exchange membrane (PEM) electrolysis is very expensive; more importantly, the global storage and production of iridium is very scarce, tremendously limiting the mass production and deployment of PEM electrolyzers. There have been a large number of non-precious metal based OER and HER studies. However, most of these studies have been performed on the rotating disk electrodes (RDEs) under alkaline solutions. Their applications in real alkaline membrane electrolyzers have been very limited.

This work will present the primary challenges associated with the realization of alkaline membrane electrolysis, which include catalyst durability, electrode design and alkaline membrane/ionomer development. First, many OER or HER catalysts demonstrating good activity in the RDE do not work for the real electrolyzer cell. Second, an optimal interaction between the ionomer and the catalyst in the electrode has not been established. Third, current commercial alkaline membrane and ionomer cannot meet the stability requirement, they decay rapidly under high operating voltage and high temperature. Furthermore, water transport in alkaline membrane electrolysis is much more complex compared to PEM water electrolysis.

The pursuit of alkaline membrane/ionomer with various chemistries and structures by a few researcher groups has rejuvenated alkaline membrane electrolysis. They will provide a better platform to test the OER or HER catalyst to enable alkaline membrane membrane electrolysis operation.

4:30 PM  *ES11.13.03  Recent Progress of PEM Water Electrolysis in DICEP Zhongang Shao; Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

PEM water electrolysis provides a sustainable solution for the production of hydrogen, and is well suited to couple with renewable energy sources such as wind and solar. Recently, the increasing desire for green energy has rekindled the interest on PEM water electrolysis. However, the performance, life expectancy and cost of PEM water electrolyzer are still the key problems restricting its large-scale commercial use. Dalian institute of chemistry physics (DICEP) has been devoted to the research and development of key material, component, stack and system for high-performance, long-life and low-cost PEM water electrolyzer. Research on electrocatalysts for oxygen evolution reaction (OER) with high activity, excellent durability and low cost is significantly important to increase the energy efficiency and stability of water electrolyzer. To synthesize Ir-based oxide electrocatalysts with high efficiency and low cost, we introduce the second less-expensive metal, including Ru, Sn and Co to fabricate Ir-Ru, Ir-Sn and Ir-Cr oxides with low Ir contents as OER electrocatalysts. Besides, a cost-effective nanoporous ultrathin film (NPUF) electrode based on nanoporous gold (NPG) with 3D interconnected nanoporosity structure and IrOx composite has been constructed to serve as oxygen electrode. A single cell performance of 1.728 V (@ 2 A cm^-2) has been achieved by NPUF electrode with a loading of IrOx and Au at 86.43 and 100.0 mg cm^-2 respectively. One of main challenge of PEM water electrolysis is the achievement of a long-term durability exceeding 100 khours. Accordingly, degradation mechanisms of membrane electrode assembly (MEA) and stack component of PEM electrolyzer deserve large attention. In DICEP, a 9-cell PEM water electrolysis stack has been developed and tested for 7800 h. The average degradation rate is 35.5 mV h^-1. The 4th MEA of the stack is offline investigated and characterized to investigate the degradation mechanism. The electron probe X-ray microanalyzer (EPMA) illustrates that Ca, Cu and Fe elements distribute in the membrane and catalyst layer of the catalyst-coated membrane (CCM). These metal cations occupy the ion exchange sites of the Nafion polymer electrolyte in the catalyst layer and membrane, which results in the increase in the anode and the cathode overpotentials. The metallic impurities are believed to originate mainly from the feed water and the components of the electrolysis unit. Fortunately, the degradation is reversible and can be almost recovered to the initial performance by using 0.5 M H_2SO_4. This indicates the performance degradation of the stack running 7800 h is mainly caused by a recoverable contamination. Nowadays, we have successfully developed a hydrogen production system with single stack to produce H_2 at a rate of 10m^3/h for more than 10 khours with a hydrogen purity of 99.99% and delivery pressure of 35 bar.

8:00 AM  *ES11.14.01  Monolithically Integrated InGaN/Si Tandem Photocathodes for Efficient and Stable Photoelectrochemical Water Splitting Zetian Mi and Srinivas Vanka; University of Michigan, Ann Arbor, Michigan, United States.

Recently, significant progress has been made in photoelectrochemical water splitting and solar hydrogen generation. For practical application, it is essential that the constituting semiconductor photocathodes can perform unassisted solar water splitting both efficiently and stably. To date, much of the research has been focused on metal-oxide, Si, and III-V semiconductor photocathodes. A double-junction photocathode, consisting of a top light absorber (energy bandgap ~1.7 eV) and a bottom light absorber (energy bandgap ~1.1 eV) promises a solar-to-hydrogen conversion efficiency up to 30%. While Si is ideally suited to serve as the bottom light absorber, it has remained challenging to identify a 1.7-2.0 eV top light absorber that is stable in harsh photocatalysis conditions. Recent studies suggest that metal-nitride photoelectrodes, e.g. InGaN possess excellent potential for semiconductor photoelectrodes. A double-junction photoelectrode, consisting of a top light absorber (energy bandgap ~1.7 eV) and a bottom light absorber (energy bandgap ~1.1 eV) promises a solar-to-hydrogen conversion efficiency up to 30%. While Si is ideally suited to serve as the bottom light absorber, it has remained challenging to identify a 1.7-2.0 eV top light absorber that is stable in harsh photocatalysis conditions. Recent studies suggest that metal-nitride photoelectrodes, e.g. InGaN possess excellent potential for unassisted solar water splitting. InGaN with an indium composition ~50% exhibits an energy bandgap ~1.75 eV and is thermodynamically stable in photoelectrochemical water splitting. In this context, we have performed a detailed investigation of the design, synthesis, and photoelectrochemical performance of InGaN/Si double-junction photocathodes. We have demonstrated that InGaN/Si photocathodes can perform unassisted solar water splitting with relatively high efficiency in 0.5 M sulfuric acid under AM1.5G one-sun illumination. Long-term stable operation (~1,000 hrs) has been demonstrated for GaN/Si photocathodes without using any extra surface protection. In this work, GaN and InGaN nanowires are grown directly on n+-Si wafer by plasma-assisted molecular beam epitaxy. The surfaces of InGaN nanostructures are tuned to be N-rich, not only for their top c-plane surfaces but also for their nonpolar lateral surfaces, which can effectively protect against corrosion. We have discovered that the conduction band offset between GaN and Si is essentially negligible, which enables the efficient extraction of photo-generated electrons from the underlying Si wafer. The GaN/Si...
Thermal Synergies in Photo-Electrochemical Fuel Processing Devices
Sophia Haussener; Ecole Polytechnique Federale de Lausanne, Switzerland, Lausanne, Switzerland.

Achieving high current densities while maintaining a high energy conversion efficiency is one of the main challenges for enhancing the competitiveness of solar fuel producing photo-electrochemical devices. I will discuss and show how thermal integration allows for an operational device at current densities and efficiencies which otherwise could not be supported.

Photocathodes in the hydrogen-evolution half-reaction of solar water splitting. The key aspect is to incorporate nanostructured density-gradient surface of GaInP photocathodes in conjunction with sulfur-based tailoring of surface atomic composition. The resulting surface-tailored GaInP photocathodes not only significantly suppressed reflection losses at the semiconductor/electrolyte interface with enhanced saturated current density from -13.3 mA/cm$^2$ to -15.2 mA/cm$^2$ but also provides a dramatically boosted electrochemical stability with lifetime over 124 hours in 0.5 M H$_2$SO$_4$ under simulated AM1.5G illumination.

Hybrid Perovskite Photo-Absorbers for Efficient Photoelectrochemical Water Splitting
Aditya Mohite; Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas, United States.

Solution-processed halide hybrid (inorganic-organic) perovskites have demonstrated an extraordinary potential for clean sustainable energy technologies and low-cost optoelectronic devices such as solar cells; light emitting diodes, detectors, sensors, ionic conductors etc. Single junction photovoltaic efficiencies have sky rocketed to 23.3% and attempts are being made to fabricate high efficiency perovskite-perovskite tandem cells. A unique advantage of halide hybrid perovskites over other photo-absorbers is that a surface protection. To realize double-junction photoelectrodes, p-type InGaN nanowires are integrated on n-GaN nanowire junction, which enables the transport of photocreated holes from the p-InGaN to the n-GaN/Si.

Surface-Tailored GaInP: Photocathodes for High Performance Solar Water Splitting
Haneed Lim$^1$, James L. Young$^2$, John F. Geisz$^3$, Daniel J. Friedman$^3$, Todd G. Deutsch$^3$ and Jongseung Yoon$^1$; 1 Mork Family Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California, United States; 2 National Renewable Energy Laboratory, Golden, Colorado, United States; 3 Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States.

Solar-driven water splitting is a promising approach that can potentially realize cost-effective hydrogen production from readily available resources on earth. Among various candidate materials, gallium indium phosphide (GaInP) represents an enabling material to serve as a top-junction in monolithically grown multijunction photodevices for ultrahigh efficiency solar water splitting. In such tandem photodevice systems, GaInP has multiple roles such as light absorption, electrocatalysis, and corrosion-protection as it is in direct contact with an electrolyte, all of which are critically important to realize high performance solar water splitting. Here we present an approach to simultaneously enhance both efficiency and stability of GaInP:photocathodes in the hydrogen-evolution half-reaction of solar water splitting. The key aspect is to incorporate nanostructured density-gradient surface of GaInP photocathodes in conjunction with sulfur-based tailoring of surface atomic composition. The resulting surface-tailored GaInP photocathodes not only significantly suppressed reflection losses at the semiconductor/electrolyte interface with enhanced saturated current density from -13.3 mA/cm$^2$ to -15.2 mA/cm$^2$ but also provides a dramatically boosted electrochemical stability with lifetime over 124 hours in 0.5 M H$_2$SO$_4$ under simulated AM1.5G illumination.

Solar Water Splitting—Surface Energy Engineering of GaP Template on Si
Pedesseau Laurent$^1$, Idaucci$^2$, Simon Charbonnier$^2$, Pascal Turban$^2$, Yoan Leger$^2$, Tony Rohel$^2$, Nicolas Bertru$^1$, Antoine Letoublon$^1$, Maxime Valette$^1$, Anne Poncher$^1$, Ludovic Largeau$^2$, Gilles Patriarche$^2$ and Charles Cornet$^2$; 1 Univ Rennes, INSA Rennes, CNRS Institut FOTON - UMR 6082, Rennes, France; 2 Univ Rennes, CNRS IPR (Institut de Physique de Rennes) – UMR 6251, Rennes, France; 3 CEMES-CNRS, Université de Toulouse UPS, TOULOUSE, France; 4 Centre de Nano sciences et de Nanotechnologies, site de Marcoussis CNRS, Université Paris Sud, Université Paris Saclay, MARCOUSSIS, France.

The hydrogen production will play a major nanoscience role in this energy transition. Recent, for water splitting context [1], [2], a demonstration of the efficiency enhancement of BiVO4 photocathode in PEC devices[3] by simply a texturing of surfaces. Moreover, in the study of the semiconductor photocatalyst material[4], GaP semiconductor appears to be a good candidate for photodevice in PEC devices[5]. One strong argument is to have at least 1.73 eV photopotential requirement for water splitting and its bandgap is larger and about 2.26 eV. In this aim of water splitting applications, we propose a surface energy engineering for a large scale textured GaP template monolithically integrated on Si. Based on experimental analysis and theory, the stability of the [114] facets is scrutinized by scanning tunneling microscopy images and also supported by density functional theory calculations. We then show that change of the surface energy for experimentally promoting the GaP(114) surface texturation can be achieved through (i) destabilizing the GaP(001) surface by using a vicinal Si substrate or through (ii) favoring the [114] facets formation by changing the group-V atmosphere above the surface on a miscut-free GaP substrate.

The nanostructures as a surface protection layer, we have demonstrated that GaN/Si photocathodes can exhibit long-term stable operation (>1,000 hr) without using any other extra surface protection. To realize double-junction photodevices, p-type InGaN nanowires are integrated on n-p Si wafer through a polarization enhanced p+/n+ GaN nanowire junction, which enables the transport of photocreated holes from the p-InGaN to the n-GaN/Si. The top InGaN nanowire arrays with an island composition ~50% has an energy bandgap ~1.75 eV and is designed to absorb sunlight in the visible spectrum, whereas the rest of the photons with wavelengths <1.1 μm are absorbed by the underlying planar Si p-n junction. The double junction InGaN/Si photocathode has $V_{OC}$ of ~2.3 V vs RHE in 0.5 M sulfuric acid. A solar-to-hydrogen conversion efficiency ~5% is measured under AM1.5G one-sun illumination.

Work is currently in progress to achieve solar-to-hydrogen conversion efficiency >10%, which, together with the long-term stability analysis will be performed and reported.
Corrosion is a ubiquitous natural process that impacts all engineering systems, occurs through many mechanisms, and has been studied extensively, especially for metals and non-metals commonly used in construction, pipelines, and shipping. Corrosion is particularly challenging for photoelectrochemical (PEC) water-splitting devices which call for immersion of multiple conductive materials (semiconductors, catalysts, membranes) in electrolytes saturated with either hydrogen or oxygen. In this talk, I will compare and contrast the typical and best practices used in photoelectrochemical stability testing with those developed by corrosion engineers, to identify practices that can be beneficially adopted by the PEC water-splitting community. I will also discuss these practices with a focus on mechanistic studies, corrosion prevention, failure analysis, and lifetime predictions for materials in corrosive environments.

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

Session Chairs: Todd Deutsch and Kimberly Papadantonakis
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 121 C
10:30 AM ES12.01.01/ES11.01.01
Development of Protocols and Standards for Low Temperature Electrolysis Katherine Ayers, Andrew Motz, Christopher Capuano and Prasanna Mani; Nel Hydrogen, Wallingford, Connecticut, United States.

Currently over 95% of hydrogen is made from fossil fuels through natural gas reforming or coal gasification. A major part of reducing carbon emissions must therefore include sources of renewable hydrogen. In addition, capture of existing carbon dioxide sources and subsequent conversion to higher value chemicals also requires a hydrogen source. Using hydrogen from traditional sources for this purpose does not make environmental sense, since the net effect is just shifting where the carbon dioxide is emitted geographically. Large scale, cost competitive sources of renewable hydrogen are critical in moving to more sustainable processes worldwide.

Low temperature electrolysis has decreased significantly in cost while increasing in scale over the last several years, and there continue to be large opportunities for additional cost reduction and performance improvements. With the advent of low cost renewable electricity, particularly in times of excess capacity when storage is most needed, electrolysis is reaching the production and cost scale to provide a viable solution. However, as research activities have increased, differences in testing conditions, reporting comparisons, cell designs, and other factors convolute data interpretation and can lead to misleading conclusions. In addition, insufficiently controlled protocols can mask effects. This talk will describe some of the complex interactions that need to be considered, and current efforts in developing community-wide tests ranging from ex-situ material screening protocols to realistic device testing. This work is part of an ongoing program across all of the major advanced water splitting technologies, the subject of this symposium and the parallel high temperature water splitting symposium.

10:45 AM ES12.01.02/ES11.01.02
Development of Protocols and Standards for Photoelectrochemical Water-Splitting Chengxiang Xiang; California Institute of Technology, Pasadena, California, United States.

Cost competitive hydrogen generation at scale using sunlight and water can play a significant role in decarbonization of our society. In recent years, photoelectrochemical (PEC) water splitting has made significant progress in materials discovery, mechanistic understanding, as well as in achieving un-precedent solar to hydrogen conversion efficiencies in the laboratory scale. To further advance this technology and reach the bench scale (0.1 kg/day) and sub-scale (2 kg/day) operational platforms, development of standard protocols and best practices for benchmarking materials and devices as a community is critical. Standardized methodologies and best practices also provide significant benefit in accelerated RD&D of advanced materials and cross-cutting efforts.

In this presentation, I will talk about recent community-based efforts in defining targets, best practices and gaps in PEC hydrogen production in HydroGEN Energy Material Network (EMN) consortium. Specific challenges related to PEC will be discussed including scale up challenges, integration challenges at the component level, lack of performance data and test protocols for photoelectrodes under real-world operating conditions and lack of fundamental understanding of photoelectrode corrosion mechanisms and accelerated test protocols. In addition, I will also present a briefly summary and status reports on lab EMN nodes/capabilities for PEC water-splitting. Key takeaways from a recent HydroGEN Benchmarking&Protocols Workshop and DOE PEC Working Group Meeting will also be discussed.

11:00 AM ES12.01.03/ES11.01.03
Framework and Test Protocols for High Temperature Electrolysis Olga Marina; Pacific Northwest National Laboratory, Richland, Washington, United States.

Hydrogen production via water electrolysis is considered to be an efficient way to smoothen the fluctuating power output of renewable energy sources and avoid oversupplies. This presentation will provide the status of the standards and protocols development for high temperature electrolysis (HTE) technology within the US DOE HydroGEN Energy Materials Network Consortium. The current material standards, advanced characterization techniques, best practices and testing protocols from screening of fundamental material properties to device level benchmarking will be discussed to address key challenges and leverage technical advancements across the different water splitting technologies.

11:15 AM ES12.01.04/ES11.01.04
Framework and Test Protocols for Solar Thermochemical Water Splitting Ellen B. Stechel; LightWorks and School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States.

This presentation will provide the status of standards and protocol development within the US DOE HydroGEN Energy Materials Network (EMN) Consortium for advanced water splitting using concentrated solar thermochemical redox cycles, generally referred to as STCH, solar thermochemical hydrogen.

Cost competitive water splitting to produce hydrogen at scale using concentrated sunlight can contribute significantly to a net CO₂ neutral society. In recent years, STCH has made significant progress. Working as a community will further advance STCH technology with a goal of reaching demonstration scales of multiple kilowatts with promising redox active materials. The development of standard protocols, definitions, metrics, best practices, and roadmaps for benchmarking materials and reactor designs is critical to accelerate progress and lower barriers for new researchers.

In this presentation, we will discuss recent HydroGEN EMN community-based efforts in defining metrics, best practices, and gaps in STCH. In addition, we will present a brief summary of EMN nodes/capabilities as well as key conclusions from a recent questionnaire and from a recent HydroGEN Benchmarking & Protocols Workshop specifically for STCH.

11:30 AM PANEL DISCUSSION

SESSION ES12.02: Redox-Active Oxides I
Session Chairs: Olga Marina and Christian Sattler
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 121 B
Solar thermal water splitting (STWS) is a promising renewable approach to converting water into hydrogen using concentrated sunlight. The central process in STWS is the high temperature reduction and oxidation of a metal oxide where $H_2$ is produced by reaction of $H_2O$ with the reduced material. For this process to be viable, the thermodynamics and kinetics of reduction and oxidation of the redox active material must produce sufficient $H_2$ at practical rates and at temperatures at which the active material is stable. In this talk we will present our results using ab initio and machine learned models to discover candidate perovskite STWS materials. This includes predicting the stability of these materials at the operating temperature, whether these materials form as perovskites and in what specific phase, the energy of oxygen vacancies and other defects that mediate the redox process, and finally the viability of these metal oxides as STWS redox materials. The Gibbs energy, $G$, determines the equilibrium conditions of chemical reactions and materials stability. Unfortunately, $G$ has been tabulated for only a small fraction of known inorganic compounds, thus impeding an analysis of whether materials are stable and synthesizable at operating conditions. We used a statistical learning approach to identify a simple and accurate descriptor to predict $G$ for stoichiometric inorganic compounds with ~50 meV/atom.

The ability to assess and compare the performance of solar thermochemical water splitting materials individually and against other materials and even to other advanced water splitting pathways is increasingly a critical need in the field of sustainable hydrogen production. Technical assessment and comparisons include evaluating mass loss of samples during thermal gravimetric analysis (TGA) in controlled oxidizing and reducing environments; the results from TGA measurements have evolved into a widely reported metric. However, the lack of universal reference materials and calibration protocols has made comparisons between materials developed at different institutions unmanageable. We are developing standard samples and testing protocols for the solar thermochemical water splitting community as part of HydroGEN, also applicable to carbon dioxide splitting, and to solar thermochemical energy storage. We report here on the synthesis of standard materials for high temperature (~1500°C) and intermediate temperature (~1200°C) applications, the development of standard testing protocols for TGA, and benchmarking of behaviors in high temperature XRD. We will cover plans for both standard material curation and availability.

There are well-established concepts for describing and understanding the gas phase dependence of defect concentrations in oxides (Brouwer diagrams, etc.). Accordingly, detailed knowledge on bulk defect concentrations has become available for many redox-active oxides. Much less clear is the effect of the gas phase on the rate of reactions taking place on oxide surfaces, for example the oxygen exchange reaction, which is required for establishing the bulk defect concentrations. Also the partial pressure (and overpotential) dependence of oxidation and reduction reactions in solid oxide fuel or electrolysis cells is often not truly understood. The empirical dependences of the corresponding reaction rates on experimental parameters may be monitored by tools such as impedance spectroscopy, current-voltage measurements, tracer diffusion or time dependent weight or color changes. However, mechanistic interpretation of the data is impeded by the fact that the gas phase not only affects adsorbates on oxides but also ionic and electronic defects in the oxides and thus several reactants.

In the first part of the talk this lack of mechanistic understanding of oxygen surface exchange reactions is addressed. It is discussed whether partial pressure dependences of reaction rates indicate the relevant species in the rate limiting step (atomic or molecular), and what can be concluded from an exponential or non-exponential shape of a current-voltage curve in an electrochemical cells with redox-active electrodes. Moreover, it is shown how surface exchange coefficients (k-factors) from impedance measurements (k') and from tracer diffusion experiments (k") usually differ. Further factors affecting the oxygen surface exchange reaction and its degradation are exemplified by measurements with appropriate tools such as in-situ impedance PLD or microelectrodes. The usefulness of measuring the chemical capacitance for analyzing the defect chemistry of electrode materials is shown.

Effects resulting from the exposure of an oxide to light are even less understood than the surface exchange kinetics of oxides. This is addressed in the second part of the talk. It is demonstrated why such an exposure to light with energy beyond the band gap can change the defect concentration in an oxide and examples are shown for $\text{SrTiO}_3$ upon UV exposure. Illumination by light is thus a forth option for changing the stoichiometry of an oxide, in addition to the well-known approaches by partial pressure variation, applying of a voltage in electrochemical cells, and enhancing the temperature in thermochemical cells.

Ceria is used widely as an oxygen exchange material due to its phase stability and facile oxygen release and uptake. The performance of ceria in particular applications depends on the oxygen vacancy formation energy. Ceria is often doped with $Zr$ to lower the oxygen vacancy formation energy, but with the exception of $Hf$, no other single dopant has been shown to significantly alter the reduction energy, though some dopant introduce intrinsic vacancies. This is because tetralental dopants are required to prevent intrinsic vacancy formation. Here we present the use of paired charge compensating dopants to engineer tetralental dopants from non-tetralental cations. Specifically, by co-doping $3+/5+$ cations into ceria, the $3+$ dopant behaves like a tetralental dopant, thereby expanding the oxygen vacancy formation energies. We show that this novel ceria doping strategy using both computational (density functional theory calculations) and experimental results within the context of solar thermochemical water splitting.
structures through the exsolution method as an alternative to impregnation, which was successfully demonstrated to control the catalysis e.g. for \((\text{La,Sr})(\text{Ti,Ni})\text{O}_3\) solid oxide fuel cell anodes.\(^3\) Through this work we explore suited perovskite compositions towards faster reduction rates and improved syngas selectivity for thermochemical redox cycles, and also compare to traditionally infiltration processed materials of same chemistry. The high surface affinity between the metallic nanoparticles and the perovskite backbone, in which they are anchored, offers relevant advantages in terms of microstructural stability for high temperature thermochemical fuel production.

In the first part of the talk we will cover the materials design guidelines that result in exsolved-perovskite structures with increased particle coverage and size distribution, exploring the chemical nature of the nanoparticles and interfaces of the cermet. Secondly, their performance for syngas production tested under chemical looping reforming cycles will be evaluated and benchmarked with state-of-the-art materials, revealing the improved syngas production performance of exsolution-promoted perovskites and the high stability of such materials under prolonged cycling.\(^5\) These results show great promise for exsolution cermet processing route in improving fuel production kinetics, syngas yields and materials stability, opening new avenues for materials design and process optimization.

References:

4:00 PM ES12.02.06
Tunable Redox-Active Metal Oxide Frameworks Alina Schimpf; UC San Diego, La Jolla, California, United States.

Metal oxides capable of supporting excess charge-carriers play an important role in current and future advancement in energy conversion and storage technologies. Colloidal semiconductor nanocrystals offer advantages of inexpensive, scalable solution-processing and size-tunable quantum properties, but structure-property elucidation can be hindered by inherent polydispersity in such materials. Polyoxometalate clusters are molecular quantum-dot analogues that can be easily reduced to contain high electron densities. Assembly of these clusters with transition-metal linkers into doped, electronically coupled arrays thus offers the opportunity to realize well-defined solid-state metal oxide materials via inexpensive, solution-phase methods. Post-synthetic modulation of electron density and the ability to tune material properties via transition metal will be discussed.

4:15 PM *ES12.02.07
Chemical and Electrochemical Stability of Perovskite Oxide Surfaces in Energy Conversion—Mechanisms and Improvements Bilge Yildiz; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

A broad range of highly active doped ternary oxides, including perovskites, are desirable materials in electrochemical energy conversion, catalysis and information processing applications. At elevated temperatures related to synthesis or operation, however, the structure and chemistry of their surfaces can deviate from the bulk. This can give rise to large variations in the kinetics of reactions taking place at their surfaces, including oxygen reduction, oxygen evolution, and splitting of \(\text{H}_2\text{O}\) and \(\text{CO}_2\). In particular, allovalent dopants introduced for improving the electronic and ionic conductivity enrich and phase separate at the surface perovskite oxides. This gives rise to detrimental effects on surface reaction kinetics in energy conversion devices such as fuel cells, electrolyzers and thermochemical \(\text{H}_2\text{O}\) and \(\text{CO}_2\) splitting. This talk will have three parts. First, the mechanisms behind such near-surface chemical evolution will be discussed. Second, the dependence of surface chemistry on environmental conditions, including temperature, gas composition, electrochemical potential and crystal orientation will be described. Third, modifications of the surface chemistry that improve electrochemical stability and activity, designed based on the governing mechanisms, will be presented. Guidelines for enabling high performance perovskite oxides in energy conversion technologies will be presented.

SESSION ES12.03: Poster Session: Redox-Active Oxides
Session Chairs: Olga Marina and Ellen Stechel
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES12.03.01
B-Site Doped Strontium Cobalt Oxides for Water Splitting via Thermochemical Redox Reactions George Wilson; Department of Materials, Imperial College London, London, United Kingdom.

The transition towards a carbon neutral economy requires the development of new technologies for the production of alternative fuels. Thermochemical redox reactions are one established low carbon method for producing fuels to be used in existing portable and stationary applications, such as fuel cells. Current efforts have sought new redox-active metal oxides that enhance the fuel production volumes and lower the high operating temperatures set by the state-of-the-art ceria-based materials (>1200 °C). Perovskites have gained the attention of the research community due to their ability to assimilate large changes in oxygen non-stoichiometry and the large number of possible compositions, leaving the field relatively unexplored. This work presents research conducted on a new family of perovskite materials for thermochemical water splitting at more industrially useful temperatures.

B-site doped strontium cobalt oxides are a promising perovskite family previously studied for IT-SOFC cathodes.\(^2\) Thermogravimetric results demonstrate topotactic reversible redox cycling in inert and oxidising environments at intermediate temperatures (480-900 °C) significantly lower than those of ceria. The large observed changes in oxygen non-stoichiometry demonstrate the potential for significant fuel production volumes, although preliminary water splitting results show only trace hydrogen production due to strontium segregation forming a surface blocking layer. Future analysis by low energy ion scattering will aim to study the effect of surface modification with less-reducible B-site cations.\(^7\) This work intends to stabilise the perovskite surface structure and achieve improved cyclability and production volumes at intermediate temperatures.


SESSION ES12.04: Redox-Active Oxides II
Session Chairs: Olga Marina and Ellen Stechel
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 121 B

8:30 AM *ES12.04.01
Tailoring Solid Oxide Cells Redox Electrode Interfaces John Irvine; School of Chemistry, University of St Andrews, St Andrews, United Kingdom.
The greatest challenge facing Solid oxide cells (SOC), in both fuel and electrolysis cell modes (i.e, SOFCs and SOECs) is to deliver high, long-lasting electrocatalytic activity while ensuring cost and time-efficient electrode manufacture. Ultimately, this can best be achieved by growing appropriate nanarchitectures under operationally relevant conditions, rather than through intricate ex situ procedures. In our approach, metal particles are grown directly from the oxide support through in situ redox exsolution. We demonstrated that by understanding and manipulating the surface chemistry of an oxide support with adequately designed bulk (non)stoichiometry, one can control the size, distribution and surface coverage of produced particles. We also revealed that the emergent particles are generally epitaxially socketed in the parent perovskite which appears to be the underlying origin of their remarkable stability, including unique resistance of Ni particles to agglomeration and to hydrocarbon coking, whilst retaining catalytic activity.

We also present the growth of a finely dispersed array of anchored metal nanoparticles via electrochemical poling on an oxide electrode, yielding a sevenfold increase in fuel cell maximum power density. Both the nannostuctures and corresponding electrochemical activity show no degradation over 150 hours of testing. These results not only prove that in operando redox treatments can yield emergent nanomaterials, which in turn deliver exceptional performance, but also provide proof of concept that electrolysis and fuel cells can be unified in a single, high performance, versatile and easily manufacturable device. This opens exciting new possibilities for simple, quasi-instantaneous production of highly active nanostructures for reinvigorating Solid oxide cells during operation.

9:00 AM ES12.04.02 In-Situ Defect Mapping of High Temperature STCH Materials in Oxidizing and Reducing Environments Robert T. Bell1, Xin Qian2, Eric Coker3, Mark Rodriguez2, Philip Parilla1, Sossina M. Haile2 and David S. Ginley1; 1National Renewable Energy Laboratory, Golden, Colorado, United States; 2Northwestern University, Evanston, Illinois, United States; 3Sandia National Laboratories, Albuquerque, New Mexico, United States.

The ultimate practicality of solar thermal chemical hydrogen production (STCH) depends on the reversibility and lifetime of the reacting materials. This necessitates an understanding of the nature of the actual defects or processes involved in these parameters. In their materials, the effective defect phase diagram encompasses a wide range of behaviors, including oxygen vacancy formation, cation site interchange, polymorphic phase transitions, and phase separation. Here we map the phase behavior of YMnO3 using high temperature in-situ XRD under a range of oxidizing and reducing environments. We will report on the observation of phase separation and change in manganese oxidation state of YMnO3 into MnO and Y2O3 at high temperatures and reducing conditions. The reversibility of this transition is evaluated during subsequent oxidizing high temperature anneals. This in-situ defect mapping is key for understanding the dynamic behavior of potential STCH materials in real thermodynamic cycling environment to establish reversibility/lifetime for STCH materials and is key early data for emerging materials.

9:15 AM ES12.04.03 The “Perovskite Playground”—Engineering Defect Chemistry in Doped Perovskite and Perovskite-Related Oxides for High Temperature Redox-Active Chemical and Electrochemical Applications Byron O’Hayre1, Michael D. Sanders1, Debora R. Barcellos1, Chuancheng Duan1, Jake Huang1, Meagan Papa1, Vladan Stevanovic1, Nitin Kumar1, Andriy Zakutayev2, Stephan Lany1, Antoine Emery3, Chris Woltverton4, Chris Borg1 and Anthony H. McDaniel1; 1Colorado School of Mines, Golden, Colorado, United States; 2Northwestern University, Evanston, Illinois, United States; 3Citrine Informatics, Palo Alto, California, United States; 4Sandia National Laboratories, Livermore, California, United States.

Perovskite oxides are of great scientific interest due to their compositional versatility and the resulting breadth of physical properties they exhibit. Perovskite oxides are widely studied for numerous applications including solid oxide fuel cells, colossal magnetoresistors, multifierroics, chemical looping, and solar thermochemical hydrogen production. Currently, there are several hundred confirmed, experimentally synthesized inorganic perovskites. However, recent density functional theory (DFT) and machine learning (ML) screening efforts suggest that there are yet hundreds more stable perovskite or perovskite-related oxides remaining to be discovered and synthesized. Furthermore, because the perovskite lattice can generally accommodate significant concentrations of various A and B-site dopants, the range of possible multi-doped, perovskite solid-solution compositions (e.g. ABO3 ~ A2A-B2B2B/O3-A and so on) is virtually limitless. With such vast degrees of compositional freedom, how can we guide the design of new perovskite compositions to target specific properties or applications of interest? In this presentation, we will discuss two application areas (solar thermochemical water splitting and intermediate temperature fuel cells) where we are combining high-throughput computation and high-throughput experiment to accelerate the search for new redox-active perovskite materials and to improve our scientific understanding of the composition-property-performance relationships that can guide future perovskite materials optimization.

For solar thermochemical hydrogen production (STCH), we have implemented a high-throughput density-functional theory (DFT) based screening strategy to identify existing and new redox-active oxides (mostly perovskite and perovskite-related) that may be promising high-temperature water-splitters based on pass/fail tests of several thermodynamic criteria. In parallel, we use high-throughput experimental screening methods to rapidly validate promising compositional spaces. Together, these techniques have enabled us to discover several promising new STCH-active oxides, including a new, previously unknown layered perovskite with remarkable water-splitting activity.

For fuel cell applications, we have recently developed a remarkable new redox-active oxide electrode based on a multi-doped perovskite, BaCo0.2Fe0.8Zr0.5Y0.5O3-δ (BCFZY4411), that catalyzes both the oxygen evolution and oxygen reduction reactions in ceramic fuel cells and electrolyzers. While this oxide exhibits excellent properties, it represents only an one point in the quaternary Co-Fe-Zr-Y space that describes the possible B-site compositions of the BCFZY system. We have begun to explore this space via high-throughput experimentation using combinatorial pulsed laser deposition coupled to high-throughput characterization tools, to allow spatially-resolved composition and property measurements of these films under various conditions. This system produces large datasets (we have already characterized more than 1,000 distinct compositions within the BCFZY system) that are particularly well-suited to an informatics approach. We have partnered with Citrine Informatics, an industry leader in materials informatics, to extract insight and construct meaningful models from these data based on a set of chemical “features” or descriptors. Initial results show that the models accurately fit and predict trends in the data, suggesting that the chemical features provide an appropriate basis set to describe these materials' behavior. We are now using these models to pinpoint the optimal composition within the BCFZY system and understand property-feature relationships.

9:45 AM ES12.04.04 Predictive Framework for Materials Synthesis Pathways—In Situ X-Ray Studies of Manganese Oxide Polymorph Formation Bor-Rong Chen1, Wenhao Sun2, Danil Kittachev1, John S. Mangum2, Vivek Thampy3, Lauren Garten3, David S. Ginley3, Brian P. Gorman4, Kevin H. Stone5, Gerhard Ceder6,7, Michael F. Toney6,8 and Laura T. Schelhas3; 1Stanford Synchrotron Radiation Lightsource, Menlo Park, California, United States; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 4Sandia National Laboratories, Livermore, California, United States; 5National Renewable Energy Laboratory, Golden, Colorado, United States; 6Citrine Informatics, Palo Alto, California, United States; 7University of California, Berkeley, Berkeley, California, United States; 8Applied Energy Programs, SLAC National Accelerator Laboratory, Menlo Park, California, United States; 9Department of Materials Science and Engineering, UC Berkeley, Berkeley, California, United States.

Computational driven design of materials has provided guidelines for designing functional oxide materials with desired properties. However, the current computational approaches are not able to predict reaction pathways passing through intermediate or metastable phases, which have the potential to exhibit desired properties. Consequently, repeated iteration is usually required to find the reaction conditions needed for realizing targeted materials, thus inhibiting the materials discovery process. To address this challenge, we combine theory and experiments to establish a framework that guides the synthesis of intermediate/metastable phases, as well as validate this framework using hydrothermal synthesis of manganese oxide [1,2], which is highly active in electrochemical reactions.

This framework has the ability to predict the multistage crystallization along reaction pathways, and the influence of particle size and solution composition on polymorph stability. In the experimental demonstration, we monitored the evolution of manganese oxide clusters and polymorphs occurring during the synthesis by using a combination of in-situ X-ray absorption spectroscopy and X-ray wide-angle scattering. Synthesis pathways with varying conditions were studied, including potassium ion concentrations and pH values.

The results demonstrated that our computed size-dependent phase diagrams capture the metastable/intermediate polymorphs to appear, the order of their appearance, and their intermediate phases can be isolated from reaction pathways by quenching the reaction, stabilizing the phases at room temperature.
Overall, this combination of computational and experimental methodology offers a more rational and systematic paradigm for targeted synthesis of metal oxides. We envision that this “synthesis by design” approach is promising for general binary and ternary oxides systems, and will contribute to the discovery of redox-active oxides.


10:00 AM BREAK

10:30 AM *ES12.04.05

A large solid-state entropy of reduction increases the thermodynamic efficiency of metal oxides for two-step thermochemical water splitting (TWS). We present a high-throughput density functional theory (HT-DFT) study of more than 11,000 oxide compounds to screen for thermodynamically favorable two-step TWS materials, and identify many materials as potential new candidates for TWS applications. In addition to the configurational entropy associated with oxygen off-stoichiometry, we also examine a different source of entropy, the on-site electronic configurational entropy arising from excitations of electrons distributed over a large number of multiplet states (as in f-electron cations). We find that this electronic entropy is sizable in all lanthanides, and reaches a maximum value of ~4.7 kB per oxygen vacancy for Ce⁴⁺ / Ce⁵⁺ reduction. The unique and large positive electronic entropy in ceria contributes to its excellent water-splitting properties.

11:00 AM *ES12.04.06
The Electronic Entropy of Charged Defect Formation and Its Impact on Thermochemical Redox Cycles Stephan Lany, National Renewable Energy Laboratory, Lakewood, Colorado, United States.

The ideal material for solar thermochemical hydrogen (STCH) generation, which has yet to be discovered, must satisfy stringent conditions for the free energy of reduction, including, in particular, a sufficiently large positive contribution from the solid-state entropy. By inverting the commonly used relationship between defect formation energy and defect concentration, it is shown here that charged defect formation causes a large electronic entropy contribution manifesting itself as the temperature dependence of the Fermi level. This result is a general feature of charged defect formation and motivates new materials design principles for solar thermochemical hydrogen production [1].

Since the total entropy (electronic, configurational, vibrational) equals the temperature dependence of the O chemical potential, the electronic contribution can help substantially to narrow the temperature window between reduction and oxidation, and to increase the H₂ yield (H₂/steam ratio) in the oxidation step. The charged defect thermodynamics description is applied to CeO₂ as a model case, using first principles calculations for the defect formation energy and the electronic structure.


11:15 AM *ES12.04.07
Phase Transitions in Polycation Oxides for Thermochemical Redox Reactions in Energy Science Anu Majumdar¹,²,³, Departments of Mechanical Engineering, Materials Science and Engineering, Stanford University, Stanford, California, United States; ²SLAC National Accelerator Laboratory, Menlo Park, California, United States.

The ability to dissociate H₂O and CO₂ to produce H₂ and CO, respectively, is vitally important in energy science because H₂ and CO are among the primary feedstocks to synthesize chemicals and fuels. This would offer the promising prospects of turning CO₂ from a liability to an asset and help decarbonize our global energy system. To achieve this, one would require processes at the Gigatonne scale, i.e. at the same order of magnitude as CO₂ emissions. It is worth noting that today’s chemical infrastructure at the Gigatonne scale relies almost exclusively on thermochemical transformations. Hence, this dominance warrants research in identifying materials and creating processes for thermochemical dissociation of H₂O and CO₂, both thermodynamically uphill reactions, that are infrastructure compatible. Motivated by this purpose and building upon past research on two-step thermochemical processes, we have been exploring a relatively new class of materials - polycation oxides - whose thermodynamics of phase transitions can be uniquely tuned and leveraged for redox activity. Based on this, we have demonstrated both H₂O and CO₂ dissociation at thermodynamic capacities often 5-10 times higher than state-of-the-art materials such as doped ceria, spinel ferrites and perovskites. Some of our discoveries defy conventional wisdom regarding concentrations of redox-active cations, but can be explained via calculations of phase diagrams. Our current work is focused on reducing the temperatures of redox reactions to make them infrastructure compatible, while understanding and tuning the kinetics to increase reaction rates, both of which critical to eventually make them cost competitive with traditional approaches. This talk will provide an overview of our research in this area.

11:45 AM ES12.04.08
The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides Michael D. Sanders¹, Anyka Bergason-Keller¹, Nitin Kumar², Jie Pan³, Debona R. Barcellos¹, Vladan Stevanovic¹, Stephan Lany¹ and Ryan O’Hayre⁴; ¹Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado, United States; ²Physics, Colorado School of Mines, Golden, Colorado, United States; ³National Renewable Energy Laboratory, Golden, Colorado, United States; ⁴National Renewable Energy Laboratory, Golden, Colorado, United States.

Solar Thermochemical Hydrogen production (STCH) technologies employing two-step metal oxide water-splitting cycles are emerging as a viable approach to renewable and sustainable solar fuels. However, materials innovations that overcome thermodynamic constraints native to the current class of solar-thermal water splitting oxides are required to increase solar utilization and process efficiency. Increasingly, the search for new STCH cycle materials has turned towards perovskite-structured oxides. Perovskites have many desirable traits, including high structural tolerance for non-stoichiometry, tunable point-defect thermodynamics, good chemical stability and a long history of application in related fields that require oxygen exchange functionality (such as solid oxide fuel cells, chemical looping, and electrochemical water splitting). While research into perovskite-based STCH materials is still in its infancy, several compounds including Sr₇La₃Mn₄Al₃O₁₄ (SLMA) and La₉Ce₅Mn₄Al₂O₁₄ (LCMA) have shown promise. However, not only is the compositional space of these quaternary cation perovskites vast (the number of elemental variations that will form solid-solutions of the type AₐA'₁₋ₐ'B'B'₀, O₁₋₂ₐ₀ is thought to be in the tens of thousands), but the same cation combinations can form different structures. Such is the case for the recently reported Ce₂Sr₃MnO₇ (CSM) layered perovskite and the related simple perovskite Sr₇Ce₅MnO₇ (SCM). The former is a Ruddlesden-Popper phase (kNi₂F₂-type) where the simple perovskite layers are separated by simple oxide rock-salt SrO layers.

In this presentation, we will discuss the results of a thermodynamic study of these two structural families. Preliminary extent-of-reduction measurements hint at different reduction behavior between the two structures, even when accounting for cation and oxygen ratio differences. Specifically, the SCM family is much easier to reduce than the RP-phase CSM. Thermogravametric techniques are employed to capture the reduction thermodynamics, including defect-reaction specific enthalpy and entropy, Δh° and Δs°, as well as the 6-dependent partial molar enthalpy and entropy of oxygen, Δh°₆ and Δs°₆. Additional DFT modeling is used to make oxygen-site specific predictions of the oxygen vacancy formation energy to explore the role of the rock-salt layers in CSM reduction.

SESSION ES12.05/ES08.01: Joint Session: Future Trends in CSP Enabled by Redox-Active Oxides
Session Chairs: Andrea Ambrosini and Anthony McDaniel
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 123
1:30 PM  *ES12.05.01/ES08.01.01  
Aluminum-Doped Strontium Ferrite Perovskites for High-Purity \textsubscript{N}_2 Accomplished with \textsubscript{O}_2 Separation from Air via Two-Step Solar Thermochemical Cycles  
H. Evan Bush, Rishabh Datta and Peter G. Loutzenhiser; Georgia Institute of Technology, Atlanta, Georgia, United States.

Separation of \textsubscript{O}_2 from air to produce a high-purity stream of \textsubscript{N}_2 is considered via the aluminum-doped strontium ferrite perovskite (SrAl\textsubscript{2}Fe\textsubscript{3}O\textsubscript{7}) reduction/oxidation reactions in a two-step solar cycle. The cycle encompasses 1) the solar-driven thermal reduction of SrAl\textsubscript{2}Fe\textsubscript{3}O\textsubscript{7}; followed by 2) the re-oxidation with \textsubscript{O}_2 from air to produce high-purity \textsubscript{N}_2. SrAl\textsubscript{2}Fe\textsubscript{3}O\textsubscript{7} samples were synthesized and doped with controlled levels of aluminum on the B-site via the sol-gel method. Thermogravimetry was used to determine the non-stoichiometry at chemical equilibrium for temperatures between 673 and 1373, gas flows between 1 and 90\% \textsubscript{O}_2--\textsubscript{Ar}, and aluminum dopant levels of between 0.0 and 0.2. A thermodynamic model based on the compound energy formalism was applied to thermogravimetric measurements to predict equilibrium non-stoichiometry as a function of temperature, \textsubscript{O}_2 partial pressure, and non-labile aluminum concentration. The predictions were used to calculate partial reaction enthalpies and standard entropies as functions of nonstoichiometry and aluminum concentration. Aluminum doping consistently increased in the enthalpy of reduction and, therefore, the oxygen affinity of the perovskite for all values of non-stoichiometry. The thermodynamic characterization was used to inform a thermodynamic cycle analysis of an ideal air separation cycle. The analysis showed that, for a solar reactor operating at 1073 K, 99\% purities were possible for oxide to air molar ratios of up to 0.8 to 1 in the air separator. The cycle efficiency showed a strongly-inverse relationship with \textsubscript{N}_2 purity. However, the addition of a recuperation stage significantly mitigated this decline. These findings will be used inform the study of more complex, concurrently or sequentially reducing B-site cations and dopants, as well as the tuning of compositions with other dopants and cycle operating conditions in future air separation cycles.

2:00 PM  *ES12.05.02/ES08.01.02  
Concentrated Solar Radiation to Power High Temperature Thermochemical Heat Storage  
Christos Agrafiotis\textsuperscript{1} and Christian Sattler\textsuperscript{1, 2}; \textsuperscript{1}Institute of Solar Research, German Aerospace Center (DLR), Koeils, Germany; \textsuperscript{2}Faculty of Mechanical Science and Engineering, Institute of Power Engineering, Professorship of Solar Fuel Production, TU Dresden, Dresden, Germany.

Recent developments in solar-thermal power generation aim as well to achieve higher temperatures to increase the efficiencies of the power cycles as to store the solar energy to enable baseload power generation from a transient energy source.

Thermochemical redox processes are an option to store large amounts of solar energy in a compact storage system. The enthalpy effects of these reversible chemical reactions can be exploited. Oxides of multivalent metals in particular, capable of being reduced and oxidized under air atmosphere with significant heat effects are perfect candidates for air-operated Concentrated Solar Power plants since in this case air can be used as both the heat transfer fluid and the reactant (\textsubscript{O}_2) and therefore can come to direct contact with the storage material (oxide).

Porous ceramic structures like honeycombs and foams are favorable for heat exchange applications, the idea of employing such structures either coated with or entirely made of a redox material like manganese oxide and cobalt oxide, as a hybrid sensible- thermochemical solar energy storage system in air-operated Concentrated Solar Power plants has been set forth and tested up to a prototype scale on DLR’s solar tower in Juelich, Germany. By cascading different redox materials heat can be stored even more efficiently than by single material systems,

2:30 PM BREAK

SESSION ES12.06/ES11.08: Joint Session: Water-Splitting Technology Directions  
Session Chairs: Katherine Ayers and Anthony McDaniel  
Wednesday Afternoon, April 24, 2019  
PCC North, 100 Level, Room 121 C

3:30 PM  *ES12.06.01/ES11.08.01  
HydroGEN Overview, Projects and the AWSM Node Capabilities  
Huyen N. Dinh\textsuperscript{1}, Katie Randolph\textsuperscript{2}, David Peterson\textsuperscript{2}, Adam Weber\textsuperscript{1}, Anthony H. McDaniel\textsuperscript{1}, Tadashi Ogitsu\textsuperscript{1}, Richard Boardman\textsuperscript{2}, Donald L. Anton\textsuperscript{1} and Eric L. Miller\textsuperscript{1}; \textsuperscript{1}National Renewable Energy Lab, Lakewood, Colorado, United States; \textsuperscript{2}Fuel Cell Technologies Office, U.S. Department of Energy- EERE, Golden, Colorado, United States; \textsuperscript{3}Lawrence Berkeley National Laboratory, Berkeley, California, United States; \textsuperscript{4}Sandia National Laboratories, Livermore, California, United States; \textsuperscript{5}Lawrence Livermore National Laboratory, Livermore, California, United States; \textsuperscript{6}Idaho National Laboratory, Idaho Falls, Idaho, United States; \textsuperscript{7}Savannah River National Laboratory, Aiken, South Carolina, United States.

HydroGEN (https://www.h2aws.org/) EMN is a six-lab consortium, led by the National Renewable Energy Laboratory (NREL). It currently comprises six core national laboratories: NREL, Sandia National Laboratory (SNL), Lawrence Berkeley National Laboratory (LBNL), Idaho National Laboratory (INL), Lawrence Livermore National Laboratory (LLNL), and Savannah River National Laboratory (SRNL). HydroGEN aims to accelerate the discovery and development advanced water splitting materials (AWSM) for sustainable, large-scale hydrogen production, in order to more effectively enable the widespread commercialization of hydrogen and fuel cell technologies. With the rollouts of fuel cell electric vehicles (FCEVs) by major automotive manufacturers underway, enabling AWs technologies for the widespread production of affordable, sustainable hydrogen becomes increasingly important.

The HydroGEN Consortium offers an extensive collection of materials research capabilities for addressing RD&D challenges in efficiency, durability and cost. Leveraging the HydroGEN Consortium’s staff of leading technical experts and broad collection of resource capabilities is expected to advance the maturity and technology readiness levels in all the advanced water splitting technologies, including advanced electrolysists (low and high temperature), photoelectrochemical (PEC) and solar thermochemical (STCH) routes. Currently, there are 20 HydroGEN seedling projects, and one project focused on benchmarking advanced water splitting technologies. These 21 new projects utilized over 40 unique capabilities across the six HydroGEN core labs, from computational modeling to material synthesis to advanced characterization. HydroGEN is indeed a national innovation ecosystem that comprises 11 national labs, 7 companies, and 30 universities. This presentation will provide an overview of the HydroGEN EMN consortium and highlight some advanced water electrolysis and PEC projects as well as a few unique HydroGEN capability nodes that the community can leverage.

4:00 PM  *ES12.06.02/ES11.08.02  
European Efforts to Accelerate the Market Introduction of Renewable Hydrogen Production  
Martin Roeb\textsuperscript{1} and Christian Sattler\textsuperscript{1, 2}; \textsuperscript{1}Institute of Solar Research, German Aerospace Center (DLR), Koeils, Germany; \textsuperscript{2}Faculty of Mechanical Science and Engineering, Institute of Power Engineering, Professorship of Solar Fuel Production, TU Dresden, Dresden, Germany.

Converting solar energy efficiently into hydrogen is a key element to develop a sustainable and affordable hydrogen economy. The presentation will give an insight in how concentrated solar radiation can be coupled into hydrogen production processes. It will discuss the benefits and challenges of using the sunlight directly instead of converting it into other energy vectors.

The main focus will be on technologies with the perspective of large scale production at very high temperatures. Therefore solar tower systems for such production processes will be presented. Additionally the components like concentrator, receiver, and reactor of the solar production plants will be described, possible locations will be discussed, and synergies with other R&D efforts on using high temperature heat will be shown. Hybrid solutions e.g. from the sulfur industry will demonstrate how concentrated solar radiation can contribute even today to actual industrial business models.

As many of the addressed processes have to be operated continuously high temperature heat storage will also be introduced. Especially thermochemical heat storage has the potential for being the ideal technology for heat provision in high temperature production processes.

The European Union is supporting the development in its research framework programs since the 1980s. However until 2002 only a few projects were carried out. Since then a continuous improvement took place which was accelerated by the implementation of the European Fuel Cell and Hydrogen Joint Undertaking in 2008. This private public partnership lead by industry is in charge to bring technologies faster into the market than research programs lead by the European Commission would. The presentation will give an overview of the actions carried out so far and the perspective of the European efforts.
Widespread adoption of inexpensive renewable-electricity sources brings with it many exciting challenges and opportunities, the most significant being an overabundance of low-cost electricity from renewables as well as cheap photovoltaics. Thus, there is an opportunity to use virtually free electrons and photovoltaics to produce fuels and chemicals using electrochemical and photoelectrochemical devices, respectively, with water as a reactant. Electrochemical hydrogen production using water electrolysis is a commercial technology, barriers remain in terms of cost and efficiency improvements for its widespread adoption; while alternative water-splitting technologies that have the long-term potential to produce inexpensive hydrogen include photoelectrochemical (PEC) approaches, are still in their infancy. In either case materials development, interface development and cell design are critical in advancing the efficiency and cost of water splitting devices. Benchmarking protocols help to identify promising materials, facilitate translation of materials from one technology readiness level to another, and can provide clear technology crossing opportunities. This talk will cover benchmarking activities performed within the HydroGEN Energy Materials Network on: low temperature electrolysis (LTE) electrocatalysts, development of benchmarking cells for photoelectrochemical (PEC) water splitting devices, and crossing opportunities between LTE and PEC with respect to the hydrogen evolution and oxygen evolution catalysts activity and durability.

**SESSION ES12.07: Redox-Active Oxides III**

Session Chairs: Christian Sattler and Ellen Stechel

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 121 B

8:30 AM *ES12.07.01*

Thermochemical Trends in ABO$_2$-Type Compounds for Solar Fuel Generation

Sessina M. Haile and Xin Qian; Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States.

Solar-driven thermochemical production of chemical fuels using redox active oxides has emerged as an attractive means for storing solar energy for use on demand. In this process a reactive oxide is cyclically exposed at high temperatures to an inert gas, which induces partial reduction of the oxide, and to an oxidizing gas of either H$_2$O or CO$_2$, which reduces the oxide, releasing H$_2$ or CO. The capacity for fuel production is dictated by the thermodynamic properties of the oxide, specifically the enthalpy and entropy of reduction. Here we report the thermodynamic properties of a range of previously unexplored ABO$_2$-type compounds and identify those with promising characteristics for efficient thermochemical fuel production.

9:00 AM ES12.07.02

Stable Proton-Conducting Solid Oxide Electrolysis Cells for Pure Hydrogen Production at Intermediate Temperatures


High temperature electrolysis of water provides an economic and efficient pathway for large-scale hydrogen production that not only utilizes steam from nuclear energy but also allows using concentrated solar energy to accelerate renewable and sustainable energy utilization. In this technical contribution, a newly developed proton conducting solid oxide electrolysis cell (SOEC) offering the opportunity of producing dry, high purity and pressured hydrogen will be presented. Experimental results pertaining to the electrochemical performance of electrochemical cells containing developed electrolyte and electrode formulations will be presented and discussed. Bulk, interface and surface morphological and chemical stability, studied using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and focused ion beam-transmission electron microscopy (FIB-TEM) techniques, for the electrodes and electrolyte will be presented. Approaches for the minimization of cell performance degradation associated with electrode poisoning will be discussed.

9:15 AM *ES12.07.03*

Solid Oxide Electrolysis Cells for Hydrogen and Synthetic Fuel Production from Renewable Energy

Anne Hauch, Ming Chen, Henrik Frandsen, Peter Vang Hendriksen, Peyman Khajavian, Rainer Küngas, Theis Skafte, Xiaofeng Tong, Martina Trini, Dordije Tripkovic, Xiufu Sun and Mogens Bjerg Mogensen; Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark; 2Haldor Topsøe AS, Kgs. Lyngby, Denmark.

Solid oxide electrolysis cells (SOECs) can efficiently convert electrical energy (e.g. surplus wind power) to energy stored in fuels such as hydrogen or other synthetic fuels. Hydrogen can be produced via steam electrolysis and synthesis gas via co-electrolysis of steam and carbon dioxide followed by catalytic reaction to produce to synthetic fuels. Furthermore, this presentation will provide an overview of the development and improvement of SOECs over the last 15 years at Risø Nat. Lab./DTU Energy. The SOEC improvements are based on a) reduction of the ohmic resistance (including that due to oxygen electrode performance), analysis of and elimination of impurities in the feed streams, optimization of processing routes and of the Ni/YSZ based fuel electrode structure. These improvements have led to a decrease in long-term degradation rate from ~40 %/kh to ~0.4 %/kh for steam electrolysis at -1 A/cm$^2$, while the initial area specific resistance has been decreased from 0.44 Ω$\cdot$m$^2$ to 0.15 Ω$\cdot$m$^2$ at -0.5 A/cm$^2$ and 750 °C. Advanced and complementary characterization techniques have been developed during these 15 years of SOEC improvements and these will be included in the talk.

Secondly, a couple of critical degradation issues for state-of-the-art SOECs will be exemplified and discussed. This includes: 1) impurity sensitivity, where even impurities in the ppb-range can play a major role in detrimental degradation of the SOECs; 2) studies of carbon deposition and its relation to the specific operation conditions and the resulting overpotential of the SOEC; 3) segregation of phases and structural changes e.g. morphology changes and electron conducting nickel in the fuel electrode; and 4) observed Ni migration in the active fuel electrode leading to significant reduction in the percolating triple-phase-boundary length and changed properties of the remaining percolating structures.

Thirdly, the last, this talk will touch upon four selected case studies illustrating on-going SOEC research. This will include: 1) New results on improved mechanical reliability of SOEC via mechanically stronger stabilized zirconia. This is obtained through modifications (decreased yttria content or Ce-Y co-doping) of the traditional 3YSZ giving rise to a significant increased fracture strength and toughness alongside improved resistance against both high and low temperature aging. 2) Interesting results on the kinetics of LSF (lanthanum-strontium-ferrite based) electrodes will be discussed. Here tremendous performance increase has been obtained through thermal cycling – and thereby surface modifications - of model LSF electrodes. Furthermore addition of iron(III) and Zr(IV) ions to the LSF electrode surfaces have shown very promising initial performance at temperatures as low as 400 °C. 3) Recently completed thorough microstructural analysis of the Ni/YSZ electrode of a pristine and a 1-year tested SOEC stack has provided new insight into the nature of microstructural changes including Ni coarsening and mobility. In this context, phase field modelling has been used for simulating the microstructure evolution of three-dimensional complex Ni/YSZ electrodes and additional studies now reveals how critical parameters and driving forces such as contact angles and fuel electrode overpotential (pO$_2$ gradients) influences e.g. Ni morphology changes and Ni migration. 4) As the degradation of the Ni/YSZ based fuel electrode is the dominating degradation issue for S-o-A SOEC on-going research activities to overcome these degradation phenomena will also be discussed. This include results from long-term testing of SOEC with pre-reduced and infiltrated Ni/YSZ electrodes as well as more explorative work on Ni-free fuel electrodes and experiments with doping of the NiO during manufacturing the fuel electrode.

9:45 AM ES12.07.04

Durability Assessment of High Temperature Electrolysis Cells

Olga Marina, Christopher Coyle, Danny Edwards and Jeffrey Stevenson; Pacific Northwest National Laboratory, Richland, Washington, United States.
Renewable electric energy has become a significant source of the nation’s electricity. However, wind and solar power technologies are intermittent and fluctuating, and have to be balanced for electric grid stability purposes. Over-generation can lead to grid congestion or “curtailment”. Relieving the grid of excess renewable electricity can be accomplished by powering a water electrolyzer to produce hydrogen. The hydrogen can be temporarily stored and then used in filling stations, industrial applications, or converted back to electricity when shortages occur. It can also be injected into the natural gas grid either directly or after methanation as “renewable fuel”. There are a number of technologies that can be used to electrolytically split water to form hydrogen. Solid oxide cells (SOC) offer the highest overall efficiency as the high operating temperature significantly reduces the amount of electrical energy required to produce the hydrogen.

The biggest challenge for SOCs is the rapid material degradation and the limited long term stability due to their high operating temperatures. This paper will discuss the degradation processes in SOC electrodes.

Multiple button cells were tested using customary SOC materials: yttria-stabilized zirconia (YSZ) electrolyte, Ni/YSZ negative electrode, and (La, Sr)MnO\textsubscript{3} (LSM)-YSZ or (La, Sr)(Co,Fe)\textsubscript{2}O\textsubscript{4} (LSCF) positive electrodes. Long-term electrochemical performance was recorded using a multichannel potentiostat over a range of operating conditions. For each cell, loss processes associated with ohmic and electrode processes were separated using electrochemical impedance spectroscopy. Open-circuit voltage was periodically recorded to verify the quality of seals in a high steam environment as well as the consistency in steam production. Following termination of electrochemical tests, LSM/YSZ surfaces and cross-sections of individual cells were analyzed using scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS).

Cells with LSM/YSZ anodes operated at higher potentials for similar H\textsubscript{2} production and degraded more rapidly when compared to cells with the LSCF electrodes. The SEM/EDS analysis revealed microstructural changes near the electrochemically active interface such as LSM/YSZ electrode delamination and embrittlement of the YSZ electrolyte. While this was consistent with the previous findings reported by other groups, our results indicate that cell failure can occur at low current densities (low oxygen flux through the electrolyte). One of the possible degradation mechanisms is the perovskite lattice expansion that leads to delamination at the oxygen evolution electrode. SOC with LSCF positive electrodes operated at 0.9 A/cm\textsuperscript{2} near or below thermoneutral voltage for over 1000 hours. Some performance degradation was observed during the initial 200 hours and was explained by an increase in polarization resistances. Subsequently, a rather stable performance (degradation rate < 0.4%/1000 hours) was observed with only a minimal increase in ohmic resistance and no changes in the electrode polarization resistances. The improved electrode stability was attributed to the presence of the ceria-based barrier layer between YSZ and LSCF that suppresses the formation of the SrZrO\textsubscript{2} phase during fabrication and is known to contribute to the anode delamination in SOC.

10:00 AM BREAK

10:30 AM *ES12.07.05 Principles of Materials Selection for Thermochemical Fuel Production Cycles Brendan Bulfin\textsuperscript{1}, Josua Vieten\textsuperscript{2}, Dorottya Guban\textsuperscript{2}, Liya Zhu\textsuperscript{2}, Patrick Huck\textsuperscript{2}, Matthew Horton\textsuperscript{2}, Martin Roeb\textsuperscript{2}, Christian Sattler\textsuperscript{3}, Kristin A. Persson\textsuperscript{2} and Aldo Steinfeld\textsuperscript{2}.

Thermochemical H\textsubscript{2} production is broken into two parts; (a) determine the redox thermodynamics of a large set of materials and add them to a database, (b) plug each materials thermodynamic properties into a simplified process model, to determine reaction conversion extents and a figure of merit such as efficiency. The performance parameters can then be used to rank the materials for a given application.

According to this methodology, a large family of perovskite solid solutions with the general composition A\textsubscript{1-x}B\textsubscript{x}M\textsubscript{y}Ni\textsubscript{1-y}O\textsubscript{2} with A = Ca, Sr and M = Ti, Mn, Fe, Co, were investigated experimentally. The redox enthalpies and entropies of these perovskites can be tuned by adjusting their composition, making them ideal for such a broad screening process. As well as an experimental screening, an even broader range of perovskites were investigated using theoretical data gathered via density functional theory (DFT) calculations. In a joint effort between the German Aerospace Center and the Lawrence Berkeley National Laboratory, the data was used to create a search engine for redox materials based upon the infrastructure of Materials Project. A thermochemical fuel production process model is also included, which can be used to rank the materials for a given set of operation parameters.

11:00 AM ES12.07.06 Perovskite-Based Thermochemical Oxygen Pumping—A Down-Stream Applicational Approach to Increase H\textsubscript{2}/CO\textsubscript{2}-Splitting Efficiency in Concentrated Solar Power Plants Mathias Pein\textsuperscript{1}, Christos Agrafiotis\textsuperscript{2}, Martin Roeb\textsuperscript{2} and Christian Sattler\textsuperscript{3}.

Thermochemical H\textsubscript{2}O and CO\textsubscript{2} splitting is a promising approach to convert and store solar energy. Further processing of the produced H\textsubscript{2} and CO via Fischer-Tropsch-Synthesis facilitates a path to renewable carbon based fuels. For efficient cycling of the active redox material (e.g. CeO\textsubscript{2}) and high solar-to-fuel efficiencies low oxygen partial pressures during reduction are a necessity. We report an approach to overcome the present energy penalties of high vacuum pumping or intensive inert-gas sweeping, using perovskite based oxides as a thermochemical oxygen pump. Our results show, that Ca-Mn-based perovskites are able to effectively increase the reduction extent of the state-of-the-art splitting material CeO\textsubscript{2} through absorption of the oxygen released by the CeO\textsubscript{2} during reduction. That offers a way to increase the efficiency of the solar-to-fuel process, while minimizing energy penalties since this application can be implemented down-stream of the main reactor in a concentrated solar power (CSP) plant. To forecast and contribute to an actual implementation of the application into a CSP plant, our work includes a study of the cyclic behavior of structural specimens offering insight to strengths, challenges and prospects concerning structural integrity of manufactured parts. This incorporates investigation on the thermal expansion, considering structural changes and expansion due to oxygen vacancy formation, and thermal stress resistance.

11:15 AM *ES12.07.07 Using SCAN+ Calculations and the Sub-Lattice Formalism to Estimate Off-Stoichiometry in Oxides Sai Gautam Gopalakrishnan and Emily A. Carter.

Using SCAN+ U calculations and the sub-lattice formalism to estimate off-stoichiometry in oxides.

Transition-metal oxides that can tolerate a large number of oxygen vacancies, specifically systems containing the redox-active Ce (CeO\textsubscript{2}), Mn (LaMnO\textsubscript{3}), and Fe (FeO\textsubscript{2}) atoms, are crucial ingredients for generating renewable fuels via two-step, oxide-based solar thermochemical (STC) reactors. However, any predictive modeling, such as using density functional theory (DFT) calculations, needs to accurately describe the energetics of redox reactions (and, subsequently, defect formation) involving transition metals, if new candidate materials are to be found. Recently, the strongly constrained and appropriately normed (SCAN) exchange-correlation (XC) functional was developed, which impressively satisfies all the 17 known constraints for the behavior of any XC functional. However, the ability of SCAN to describe redox energies involving transition metal atoms thus far has remained unexplored. Hence, in the first part of the talk, we will explore the need for a Hubbard U correction, along with SCAN, to account for some of the discrepancies in the thermodynamic and electronic properties of transition-metal and rare-earth oxides.

Importantly, theoretical models that can accurately predict the extent of off-stoichiometry, i.e., the extent of oxygen deficiency within the oxide, will be crucial in identifying promising candidates for STC applications. Thus, the second part of the talk will focus on using the sub-lattice formalism in combination with SCAN+ U calculations to accurately predict off-stoichiometries in CeO\textsubscript{2} and Zr-doped CeO\textsubscript{2}. Note that the sub-lattice formalism is a common tool used to thermodynamically assess experimental data and build
temperature-composition phase diagrams in a variety of binary, ternary, quaternary, etc. systems. Although the sub-lattice model has been primarily used to "fit" to existing experimental data, the framework is general and can be used alongside DFT-based data. Hence, we build a sub-lattice model entirely based on SCAN+U calculations and observe fair agreement between experimental and predicted oxygen off-stoichiometries in CeO$_2$ and Zr-doped CeO$_2$. Finally, we will touch upon some of the future challenges in generalizing the use of sub-lattice models across chemical systems.

11:45 AM ES12.07.08
Study of the Reduction Thermodynamics of Sr$_{1-x}$Ce$_x$MnO$_3$ Perovskites for Solar Thermochemical Hydrogen Production
Anyka Bergeson-Keller, Debora R. Barcellos, Michael Sanders and Ryan O'Hayre; Colorado School of Mines, Golden, Colorado, United States.

Solar Thermochemical Hydrogen Production (STCH) is an emerging technology that uses concentrated solar heat to split water and produce hydrogen. STCH leverages the ability of some transition metal oxides to reversibly change their oxygen stoichiometry with changes in temperature and oxygen partial pressure. The potential impact of this technique is significant because it enables the use of solar radiation as a carbon-free energy source to produce industrial scale quantities of hydrogen, which is widely used in steel production, ammonia synthesis for fertilizers, and as an alternative renewable fuel.

The high reduction temperatures necessary for the current state-of-the-art STCH material, CeO$_2$ (ceria), results in solar utilization and process efficiencies that are too low for practical application, leading to a broad effort to replace it. However, the thermodynamic constraints of lowering the reduction temperature while retaining a defect formation energy large enough to facilitate water splitting is challenging. The tunable point-defect thermodynamics, good chemical stability, and structural tolerance for non-stoichiometry inherent in transition-metal perovskite oxides makes them attractive candidates. The recent development of Sr$_x$La$_{1-x}$MnO$_{3-δ}$ (SLMA) and BaCe$_0.25$Mn$_0.75$O$_3$ (BCM) as active STCH oxides demonstrate the potential of the perovskite materials space for this application.

Following the success of BCM, a Sr-containing variant has been synthesized, Sr$_{1-x}$Ce$_x$MnO$_3$ (SCM). Unlike BCM, the SCM family contains Ce on the A-site and it is not a line compound, instead accommodating a wide compositional range of approximately 0-50% Ce substitution. This allows for a level of defect tunability that is not possible in BCM.

For this work, we discuss the results of a thermodynamic study of this compositional family and the effects of Ce content on thermal reduction. Thermogravimetric techniques are employed to capture the reduction thermodynamics, including defect-reaction specific enthalpy and entropy, Δh° i and Δs° i, as well as the δ-dependent partial molar enthalpy and entropy of oxygen, Δh° O and Δs° O. Extent of reduction and water-splitting hydrogen production results will also be shared.

SESSION ES12.08: Redox-Active Oxides IV
Session Chairs: Olga Marina and Christian Sattler
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 121 B

1:30 PM ES12.08.01
Development of Solid-Oxide Fuel-Cell Stacks Based on Proton-Conducting Ceramics
Long Q. Le$^1$, Hanping Ding$^1$, Liangzhu Zhu$^4$, Carolina Herradon Hernandez$^2$ and Neal P. Sullivan$^1$; $^1$Mechanical Engineering Department, Colorado School of Mines, Golden, Colorado, United States; $^2$Department of Engineering Science, Universidad Andrés Bello, Santiago, Chile; $^4$Idaho National Laboratory, Idaho Falls, Idaho, United States; $^3$Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, Colorado, United States.

In this paper, we present our efforts to scale up proton-conducting ceramic fuel cells (PCFC) into small stacks. Encouraging stack performance is observed under hydrogen and methane fuels at intermediate temperatures. The membrane-electrode assembly features a BaCe$_{0.25}$Zr$_{0.75}$Y$_{0.25}$O$_{3+δ}$ (BCZYZ) electrolyte on a Ni-BCZY26 anode support. The cathode material is BaCe$_0.25$Fe$_{0.75}$Zr$_{0.25}$O$_{3+δ}$ (BCFY), with mixed ionic-electronic conduction, enabling high performance at 550 °C. Cell active area is ~ 5 cm$^2$. The cells are packaged within ThyssenKrupp’s Crofer 22 APU ferritic-steel interconnects. A three-cell stack operating at 550 °C under internally reformed methane-steam fuel achieved 0.25 A / cm$^2$ at 11:45 AM.

Stack development brings concerns of materials compatibility, mating novel proton-conducting ceramics with high-chrome ferritic steels and glass-ceramic sealants. While lower operating temperature should reduce degradation rates, it also brings questions on scale composition, materials interactions, and other sources of performance degradation. In an effort to gain insight on root causes behind degradation in our protonic-ceramic stacks, we distribute numerous voltage taps throughout the electrical interfaces across the unit-cell stack. We trace stack degradation to an increase in electrical resistance across the cathode interconnect. Following testing, this interconnect displays a scale with high iron content, rather than the desired (Mn,Cr)$_2$O$_3$ scale. We present early results on the effectiveness of interconnect pre-oxidation in reducing degradation. We also explore stack performance when using Sandvik’s SANERGY 441 interconnect, with and without protective Ce-Co coatings.

1:45 PM ES12.08.02
Electrode Degradation in Proton-Conducting Ceramic Fuel Cells and Electrolyzers
Marcos Hernandez Rodriguez$^1$, Long Q. Le$^1$, Liangzhu Zhu$^1$, Carolina Herradon Hernandez$^2$, Max Pisciotta$^3$ and Neal P. Sullivan$^1$; $^1$Colorado School of Mines, Golden, Colorado, United States; $^2$Department of Engineering Science, Universidad Andrés Bello, Santiago, Chile.

In this paper, we present our efforts to identify, quantify and mitigate sources of degradation in proton-conducting ceramic electrochemical devices. Proton-conducting ceramic membranes present an exciting new class of electrochemical materials that are now being harnessed to address societal challenges in electricity generation, energy storage, and fuels synthesis. Many materials-compatibility questions arise as we move protonic ceramics from lab-scale, “button cell” architecture to commercial kW-scale assemblies. For the first time, we are packaging protonic ceramics within multi-cell stacks, mating novel perovskites with high-chrome ferritic-steels and advanced glass materials. The compatibility and stability of these materials within tightly packaged assemblies over thousands of hours of operation is unclear. Additionally, the unique operating conditions found with protonic ceramics differ substantially from those for which the packaging materials were initially designed. Both fuel cells and electrolyzers based on protonic-ceramics feature high water-vapor content at the air / steam electrode. Operating temperatures may be 200 °C lower than that of the oxygen-ion-conducting equivalent. While this lower-temperature operation should be beneficial for long-term operation, many questions remain.

In this talk, we present our approaches to capturing degradation effects at the protonic-ceramic air / steam electrode. We have developed precise experimental tools and fabrication protocols to accurately quantify the small performance changes that may be manifested over thousands of hours operation. We utilize symmetric cells for these experiments, where a BaCe$_{0.25}$Zr$_{0.75}$Y$_{0.25}$O$_{3+δ}$ (BCZYZb) electrolyte is sandwiched between BaCe$_{0.25}$Zr$_{0.75}$Y$_{0.25}$O$_{3+δ}$ (BCFY) air-stem electrodes, and exposed to steam-air mixtures at −550 °C. In addition to identifying stable operating conditions, we are exploring the compatibility of commercial ferritic steels, such as ThyssenKrupp’s Crofer 22 H and Sandvik’s SANERGY 441 materials, with these novel protonic-ceramic materials. Experiments are executed under continuous potentiostatic electrochemical impedance spectroscopy (EIS) through a Gamry Reference 600 instrument. While degradation is found to be high at 50% steam in air, far-lower degradation is observed at 10% steam. Preliminary results reveal...
that packaging of symmetric cells within uncoated, untreated ferritic steels can lead to substantial performance degradation. We will also present on the effectiveness of degradation-mitigation strategies to enable long device lifetime.

2:00 PM ES12.08.03
Ammonia Synthesis in Two Cyclic Steps—Basic Thermodynamic Considerations James E. Miller1, Ivan Ermanoski2, Andrea Ambrosini2 and Ellen B. Stechel1; 1Arizona State University LightWorks®, Tempe, Arizona, United States; 2Sandia National Laboratories, Albuquerque, New Mexico, United States.

The fossil fuel based production of ammonia, NH3, is essential to the modern agricultural endeavor that sustains humanity. However, a combination of kinetic and thermodynamic considerations drives the current industrial process to high pressures and moderately high temperatures. Furthermore, the process is net carbon intensive. Thus, more sustainable alternatives will be needed. Following the model of thermochemical approaches to water splitting for H2 production, one potential option is to accomplish the conversion by dividing the desired reaction into multiple steps. However, the typical understanding of thermochemical cycles does not directly map onto the ammonia production step. Typically, thermochemical cycles apply to difficult endothermic reactions, which are thermodynamically unfavorable at moderate conditions of temperature and pressure. The ammonia production from hydrogen and nitrogen is exothermic and quite thermodynamically favorable at low temperatures. The implications of this difference as well as other basic thermodynamic considerations for producing ammonia from H2 and N2 in two cyclically-repeated steps will introduced and discussed.

2:15 PM ES12.08.04

Ammonia is an important industrial precursor [1] and a promising energy carrier due to its low liquefaction pressure. In this paper, we report high electrochemical ammonia-synthesis rates using proton-conducting ceramics with nitrogen and steam feedstocks. Ammonia synthesis is enabled through use of a novel barium-calcium-aluminum oxide support with a low-loading ruthenium catalyst (Ru-B2CA) [2]. This catalyst and support have been patented by Starfire Energy, Denver, Colorado, USA, for both ammonia synthesis and ammonia cracking. The matting of protonic-ceramic electrochemical cells with advanced Ru-B2CA catalysts enables efficient, cost-effective storage of intermittent renewable electricity in the form of a commodity chemical. The cell-catalyst system is also reversible, and demonstrates high power density under ammonia fuel.

The protonic-ceramic electrochemical cells feature a BaCe0.8Zr0.2Y2O3-δ (BCZY) electrolyte on a Ni-BZY fuel-electrode-support, and BaCo0.8Fe0.2O3-δ (BCZFO) air-electrode steam. These solid-state electrochemical-synthesis processes, we achieved an ammonia production rate of \(1.0 \times 10^4\) mol.s\(^{-1}\) at ambient pressure from steam (carried by humidified air) and nitrogen feed streams. This rate is among the highest electrochemical ammonia-production rates ever reported, regardless of electrolyte type [3-6]. Other reported rates reach 1.1 \(\times 10^6\) mol.s\(^{-1}\) using Nafion electrolyte and SFCN as ammonia formation catalyst [3], and 1.0 \(\times 10^4\) mol.s\(^{-1}\) using molten NaOH-KOH as electrolyte and nano-Fe2O3 as catalyst [4]. An ammonia-production rate of 8.2 \(\times 10^4\) mol.s\(^{-1}\) has been reported using GDC electrolyte and Ag-Pd catalyst [5]. The effects of cell architecture, operating temperature and pressure on ammonia-synthesis rate will be discussed in this talk.

2:30 PM ES12.08.05

Solar-thermochromic (STC) carbon dioxide and water splitting is a pathway for the direct thermal production of solar fuels—an alternative to direct thermolysis. Currently, the most widely researched implementation is the two-step cycle. Reducing two–step cycles to practice is challenging, and there is a substantial ongoing effort to improve reactor designs, and to synthesize redox active materials that exceed the STC potential of ceria, the current state–of–the–art redox active material. We have analyzed the underlying general thermodynamic boundaries that lead to materials performance tradeoffs between heat of reduction, productivity, and yield. These boundaries apply to all nonstoichiometric oxides without phase changes during redox cycles, or where the phase changes are energetically negligible. We quantify the tradeoffs between the desirable decrease of the heat of reduction and penalties such as decreasing yields and increasing cycling temperature range, and show that operating parameters pose firm limitations on cycle performance and on the desirable materials properties space.

2:45 PM ES12.08.06
Nanostructured Ceria Based All-Oxide Electrodes as the Key to Efficient and Robust High-Temperature Energy Storage Technology Christopher Graves1, 2, 3; 1Department of Energy Conversion & Storage, Technical University of Denmark, Roskilde, Denmark; 2Noon Energy Inc., Berkeley, California, United States; 3Cyclotron Road Fellow at Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Solid oxide electrochemical cells have the potential to play a major role in our renewable energy future. They efficiently store electrical energy as synthetic chemical fuels such as H2, CO and hydrocarbons by electrolysis of H2O and/or CO2. They can also operate as fuel cells to produce electricity again from those fuels. By reversible operation between electrolysis and fuel-cell modes, they can function as rechargeable flow batteries with extremely low cost storage media.

A major obstacle to commercialization is insufficient device lifetime due to loss of electrode performance. Nearly all cells employ nickel-based fuel-electrodes, which experience gradual deactivation - mainly due to the mobility of nickel - and can even be completely destroyed by oxidation or carbon deposition. Alternative electrodes made of mixed ionic-electronic conductor (MIEC) oxides are known to avoid these issues, but at the expense of typically much lower electrochemical activity.

We have been developing nanostructured ceria-based fuel-electrodes that overcome these issues and outperform conventional nickel-based electrodes. In the H2/H20/CO/CO2 fuel environment, acceptor-doped ceria is a MIEC with a high concentration of oxygen vacancies, which provide a high density of surface reaction sites. This presentation will focus on how these electrodes achieve:
- exceptional activity: electrode polarization resistance <0.1 ohm cm\(^2\) at 650°C
- exceptional stability: inhibiting carbon deposition even during CO2 electrolysis in thermodynamic carbon deposition conditions, as well as the ability to re-activate electrode performance by periodically shifting to oxidizing conditions and back again

3:00 PM ES12.08.07
Stabilization of Brownmillerite SrCoO\(_3\) for Oxygen Enrichment Applications Aswathy M. N, Rajasekar Parasuraman and Arun M. Umarji; Indian Institute of Science, Bengaluru, India.

Mixed ionic-electronic conducting (MIEC) oxide ceramics are grabbing attention towards a variety of applications such as oxygen sensors, catalyst bed for combustion of fossil fuels, cathodes for solid oxide fuel cells, oxygen separation membranes, oxygen storage devices etc. These MIECs can transport oxide ions through their lattice when an oxygen partial pressure gradient is applied across the material\(^2\). They also have reversible oxygen storage capabilities at elevated temperatures. Transition metal Perovskite oxides (general
thermal–driven pumping approach has the potential to substantially exceed state-of-the-art pumping efficiencies, especially in the low-pressure regime, in inherently simple and potentially low-cost devices.

SYMPOSIUM ES09

Advanced Materials for the Water-Energy Nexus
April 23 - April 25, 2019

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* Invited Paper

SESSION ES09.01: Batteries I
Session Chairs: Veronica Augustyn and Roland Cusick
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 131 A

10:30 AM ES09.01.01
Manganese Oxides—Functional Electrochemistry and Insight into Their Redox Mechanisms Esther S. Takeuchi, Amy C. Marschilok and Kenneth Takeuchi; Stony Brook Univ, Stony Brook, New York, United States.

Manganese oxides are a structurally rich class of materials and can be prepared as layered, tunneled, or spinel structured materials. The synthetic versatility of these materials is further expanded as they are often prepared with cations as part of the structures including univalent cations such as K\(^+\), Ag\(^+\), or Na\(^+\), Rb\(^+\), or Cs\(^+\) or multivalent cations such as, Ni\(^2+\), Cu\(^2+\), Co\(^2+\), Mg\(^2+\), or Al\(^3+\). The ability to deliberately tune both the structure and the composition of the materials has led to investigation of their functional behavior for a number of applications as both the parent structure as well as the nature of the cation can be determining factors. The interest in manganese oxide materials is further enhanced by their relatively low cost and toxicity.

This presentation will explore the electrochemistry of manganese oxides in lithium, sodium and magnesium based electrolytes for possible application in electrochemical energy storage devices. Examples of layered, tunneled and spinel manganese oxide structures will be considered. Discussion will include the functional electrochemistry as well as insight into the reduction and oxidation mechanisms.

11:00 AM ES09.01.02
Toward a Low-Cost High-Voltage Sodium Aqueous Battery Kiosik Kang; Seoul National University, Seoul, Korea (the Republic of).

Highly concentrated aqueous batteries have emerged as potential candidates for large-scale energy storage applications; however, the need for high-cost organic electrolyte salts is a potential obstacle hindering their practical application. Herein, we revisited all the commonly used low-cost inorganic electrolytes and discovered that the use of low-cost super-
concentrated aqueous solution result in a high electrochemical stability window of up to 2.7 V by suppressing water dissolution and induces stable solid-electrolyte interphase (SEI) layer formation without involving the reduction of salt anions. The SEI layer, composed of Na$_2$CO$_3$ and Na–O compounds, guarantees the excellent electrochemical storage stability of the full-cell composed of a Na$_2$Fe$_3$(PO$_4$)$_2$(P$_2$O$_7$) cathode and NaTi$_2$PO$_4$ anode for over 890 hours. This new-class 2-V Na-ion battery provides remarkable cycle stability and a Coulombic efficiency of over 99% at 1C for over 200 cycles.


The Advanced Electrochemical Materials section at the U.S. Naval Research Laboratory has designed and validated a three-dimensional (3D), monolithic Zn electrode architecture that solves the limited rechargeability of Zn. We use a simple emulsion-based protocol to produce moldable, scalable, Zn “sponge” electrodes whose structural characteristics impart: (i) interconnected pathways that maintain long-range electronic conductivity within the electrode volume throughout charge-discharge; (ii) an electrified 3D interface that imparts more uniform current distribution; and (iii) confined internal void volume that controls Zn/Zn$^{2+}$ precipitation/dissolution dynamics and product redistribution.

These Zn “sponge” anodes exhibit unprecedented cyclability at high depths-of-discharge (theoretical DOD$_{max}$), increased specific capacity relative to conventional powder-bed Zn electrodes, and tens of thousands of cycles with low-DODZn pulse-power profiles, as recently demonstrated in prototype Ni–Zn cells. This breakthrough enables the entire family of alkaline Zn batteries (Ni–Zn, Ag–Zn, MnO$_2$–Zn, and Zn–air) plus neutral pH zinc-ion batteries to be reconfigured in extensively rechargeable forms, with energy and power characteristics that are competitive with Li-ion batteries. Our second-generation emulsion protocol improves the volumetric density of the sponge thereby concomitantly improving the energy density of the cell while adding mechanical ruggedness to the anode. The potential paths forward for the development and transition of this safer energy-storage technology will be discussed.

SESSION ES09.02: Water Desalination I
Session Chairs: Roland Cusick and Matthew Suss
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 131 A

1:30 PM *ES09.02.01 Material Requirements for Capacitive Deionization Electrodes Michael Stadermann$^1$, Steven A. Hawks$^1$, Ashwin Ramachandran$^1$, Ali Hemmatifar$^2$, Patrick G. Campbell$^3$ and Juan G. Santiago$^4$; $^1$Lawrence Livermore National Laboratory, Livermore, California, United States; $^2$Stanford University, Palo Alto, California, United States.

Capacitive deionization (CDI) is a promising technique for water treatment. At the heart of every CDI device are the electrodes that adsorb ions from the liquid. Much of the improvement of CDI performance in the past decade has focused on increasing the sorption capacity of the electrodes.

Here, we will present our latest results on optimizing device operation, charge efficiency and thermodynamic efficiency, and the impact of these results on future electrode material and performance characterization. Specifically, we will break down the overall charge efficiency into double-layer efficiency, flow efficiency, and Coulombic efficiency and show how the choice of material, morphology, and operating conditions affects each of these efficiencies, and highlight how measured salt adsorption capacity (SAC) depends on the charge efficiency. We will demonstrate a simple way to optimize operational parameters for a specific separation and show that for a given separation the impact on SAC on performance can be limited. We will show the impact of electrode dimension on the device power consumption and thermodynamic efficiency. Our findings suggest that optimization of shape and morphology of the material play as important a role as the intrinsic capacity of the material for future CDI electrode development.

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

2:00 PM *ES09.02.02 Rational Electrode Design and Device Operation for Enhanced Performance and Durability of Electrochemical Desalination Processes in Complex Waters Meagan Mauter; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Capacitive deionization based on carbonaceous electrodes represents an energy-efficient technology suitable for low-salinity brackish water desalination where high recovery rates are critical to economic viability. Substituting insertion compounds for carbonaceous materials in electrochemical desalination electrodes enables higher ion adsorption capacities, excellent energy efficiency in higher salinity feedwaters, and selective removal of target ions. These insertion electrode properties introduce a novel set of process applications and advantages in deploying electrochemical separations, including the selective recovery of high value byproducts from reverse osmosis concentrate and reduced energy consumption and environmental impacts associated with efficient removal of target ions of environmental concern.

Despite the promise of carbon and insertion based electrochemical desalination processes, the durability of the electrode materials when treating complex waters is a documented issue that has not been systematically investigated. This presentation will review our ongoing work to examine the impact of organic fouling on the performance of carbonaceous and insertion-based electrochemical desalination processes, identify key factors controlling the corrosion/degradation of carbonaceous and insertion-based electrodes used in electrochemical desalination, and explore and assess cost-effective strategies for improving the fouling tolerance and minimizing the corrosion or degradation of carbonaceous and insertion-based electrodes.

2:30 PM ES09.02.03 Global Sensitivity Analysis to Assess Performance and Characterize Operational Limitations Across Capacitive Deionization Technologies Steven M. Hand$^1$, Xia Shang$^2$, Jeremy Guest$^1$, Kyle Smith$^1, 3, 4$ and Roland Cusick$^1$; $^1$Civil & Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; $^2$Mechanical & Engineering Science, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; $^3$Beckman Institute for Advanced Study, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; $^4$Computational Science and Engineering Program, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Capacitive deionization (CDI) is a class of electrochemical desalination technologies which typically desalinate via ion storage in electric double-layers. CDI has received attention in recent years due to the ability to couple energy storage with salt separation. Unlike reverse osmosis (RO), a portion of the energy applied during desalination can be recovered directly as electrical energy, reducing net energy consumption. Apart from the thermodynamic minimum energy of separation, all energy applied should be recoverable.

However, in practice, ion/electronic resistances, inefficient hydraulic design, parasitic reactions, and poor selectivity limit the portion of energy recoverable. Several material additions and electrode configurations have been proposed to overcome these limitations. Two of the most prominent modifications are the addition of ion exchange membranes (IEMs), promote counter ion flux out of the desalination chamber, and utilizing flowable, carbon slurry electrodes, to increase salt removal capacity. Likewise, functionalization of carbon electrodes has been used to improve counter-ion adsorption within EDL micropores. While the incorporation of IEMs in membrane capacitive deionization (MCDI), the use of slurry electrodes in flow capacitive deionization (FCDI), and the incorporation of functionalized carbon have successfully reduced energy consumption or increased ion adsorption capacity in CDI systems, these modifications are often evaluated under limited conditions on the basis of specific performance enhancements. Further, evaluation of practical CDI performance has been limited by low reported experimental salinity reduction (the concentration difference between influent and effluent charging is typically 10 mM or less). Additional clarity is necessary to evaluate the associated performance and cost tradeoffs across the design space.

In this study, a porous electrode (M/F)CDI model was used to measure the sensitivity of CDI performance to across the design landscape of architectural, material, and operational inputs. In order to investigate the performance of FCDI, pulse-flowed electrodes of high capacity and electronic resistances were incorporated into the existing model. Similarly,
fixed charge in the anodic and cathodic micropores was studied to investigate functionalized carbon. Sensitivity for CDI, MCDI, and FCDI were evaluated by varying eight common input parameters. Sensitivity analyses were conductions using both Monte Carlo and Morris methods utilizing six common performance metrics (salt adsorption capacity [SAC], average salt adsorption rate [ASAR], energy-normalized adsorbed salt [ENAS], charge efficiency [l+ or n2+], and round-trip efficiency/energy recovery [r2+n2+], and thermodynamic efficiency [η]).

Our sensitivity analyses show that operating current density, electrode specific capacitance, and contact resistance were the parameters which most significantly dictated (M/F)CDI performance. Both CDI and FCDI were out performed by MCDI, due to relatively poor charge and round-trip efficiencies, respectively. We found that increased system performance across most metrics was associated with input parameters which increased charging cycle duration. Lastly, simulated MCDI achieved thermodynamic efficiency comparable to brackish water RO, although tradeoffs exist between water recovery and thermodynamic efficiency.

2:45 PM ES09.02.04 Cooperative Effects in Molecular Dynamics of Water Confined in Hydrophobic and Hydrophilic Nanopores Margarita Russina and Veronika Grzimek; EM-ISFM, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

The molecular dynamics of confined of water is important for many areas of science and applications ranging from energy storage to transport phenomena in geology and biology. In this context, the understanding of hydrogen bonds formation in various environment and criteria governing the molecular mobility at nanoscale is of high importance. Using neutron spectrometer NEAT as a powerful magnifying glass we have investigated molecular dynamics of water in hydrophobic and hydrophilic nanocolumn in a very broad temperature range of 20-300 K. By an aimed selection of the confining systems we were able to follow the molecular behavior in pores of various sizes and shapes and in environments with variable degrees of water host interactions. Changing the amount of confined water we have studied the process of hydrogen bonds formation and were able to explain the molecular mechanism of adsorption behavior in selected hydrophobic systems. Thus in zeolite Al(PO₄)₃ with hydrophobic one-dimensional channels of about 1 nm cross section we observed non-monotonous behavior of the mean square displacement as amount of confined water increases. The cooperative interactions between water-water molecules lead to the increase of molecular mobility and the sharp rise in water intake. Guest-host interactions initiate adsorption-induced changes of the host structure, which in the case of Al(PO₄)₃ cause the anisotropic contraction of the zeolite framework. These structural changes can be the reason for a broad isotherm hysteresis observed in this system.

3:00 PM BREAK

SESSION ES09.03: Electrochemical Capacitors
Session Chairs: Majid Beidaghi and Matthew Suss
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 131A

3:30 PM *ES09.03.01 Two-Dimensional Carbides and Nitrides (MXenes) for Water Purification and Electrochemical Energy Storage Samantha Buzcek,1 Ravi P. Pandey2, Abdul R. Pathath2, Khasif Rasool2, Ekaterina Pomerantseva1, Khaled A. Mahmoud2 and Yury Gogotsi1; 1Material Science & Engineering, Drexel University, Philadelphia, Pennsylvania, United States; 2Hamad Bin Khalifa University, Ar Rayyan, Qatar.

Nanomaterials have attracted significant attention by researchers over the past decade towards developing sustainable technologies. MXenes, a large family of two-dimensional (2D) transition metal carbides and nitrides, are the front runners of 2D material research due to their diverse physiochemical properties. MXenes are synthesized by wet chemical etching of an atomic layer from layered ternary carbide precursors (MAX phases), resulting in terminations (-O,-F,-OH) on the surface. Their unique combination of hydrophilicity and metallic conductivity, enable compatible solution processing of conductive MXene materials by various methods in scalable quantities. MXenes can be dispersed in aqueous and organic solvents to make colloidal, functional solutions which can be subsequently prossessed via printing, spray coating, drop casting, or vacuum filtration for the rational design of devices with different architectures. The 2D morphology, diverse transition metal chemistry, and functionality offered by MXene materials has spurred their use in a wide range of applications, specifically energy storage and water purification. The ability of MXenes to spontaneously intercalate a variety of cations and/or large organic molecules has created the platform for efficient storage or removal of guest species. Fast redox reactions at the transition metal-oxide/hydroxide-like surfaces with efficient charge transfer due to high electronic conductivity, makes MXenes a promising candidate as high rate pseudocapacitive materials for energy storage applications. Furthermore, combination of slit-like pores with electronic conductivity, qualifies MXenes as capacitive deionization (CDI) electrodes for efficient and reversible removal of ionic species/organic molecules from brackish water. In addition, membranes composed of Ti2C nanosheets have already shown potential in selectively sieving gases, such as H2 and various alkali, alkaline earth ions (Li+, Na+, K+, Mg2+, Ca2+), metals (Ni2+ and Al3+), and dye cations (MB) based on charge and size without sacrificing water flux rate. The high aspect ratio of the flakes allows for the fabrication of membranes with uniform and narrow 2D nanochannels. Systematic studies of the effect of interlayer spacing and surface functionalization on the transport of ions in confined channels can provide valuable insight to progress use of MXene in the fields of energy storage and water purification.

4:00 PM *ES09.03.02 High Performance Carbon/Carbon Electrochemical Capacitors Implementing Concentrated Aqueous Electrolytes Patryk Przygocki, Qamar Abbas, Barbara Gorska and Francois Beguin; Poznan University of Technology, Poznan, Poland.

In order to reach high voltage and high energy density, electrochemical capacitors (ECs) with activated carbon (AC) electrodes mostly implement organic electrolytes. Due to the relatively poor environment friendliness and high cost of these devices, developing ECs with alternative electrolytes is highly demanded. AC electrodes in aqueous solutions with pH close to 7 have been shown recently to display enlarged potential window compared to classical electrolytes as H2SO4 or KOH. The window is extended under negative polarization owing to water reduction and production of hydroxy groups (OH-), which leads to a pH increase inside the porosity of the AC electrode and consecutive downsfting of the Nernst di-hydrogen evolution potential. Hence, when using stainless steel current collectors and alkali sulfate solutions, practical voltage values of 1.5 V are reached. Besides, enhanced capacitance was demonstrated when hybrid AC/AC capacitors comprising a faradic positive electrode and an electrical double-layer (EDL) negative electrode are realized by implementing an aqueous solution of potassium iodide. Subsequently, bi-functional electrolytes containing Li2SO4 as negative electrode potential range extender and KI as promoter of battery-like positive electrode have been proposed to enhance cell voltage and capacitance, respectively, allowing the energy of the thereof realized hybrid EC in aqueous ChNO3 to be increased down to -40°C. Based on this success, we now propose a bi-functional electrolyte containing 5 mol kg⁻¹ LiTFSI or Li2SO4, causing advantageously a voltage extension by ca. 200 mV. Despite these advantages of water-in-liquid electrolytes, the solutions display a very low conductivity and the ECs performance quickly fades when lowering temperature down to -20°C. Recently, we have implemented a new family of concentrated (5 mol kg⁻¹) aqueous electrolytes based on choline chloride, owing to which symmetric ECs demonstrated excellent performance down to ~40°C. Based on this success, we now propose a bi-functional electrolyte containing 5 mol kg⁻¹ choline nitrate (ChNO3), as supporting neutral electrolyte providing low potential extension for the negative electrode, and 0.5 mol kg⁻¹ choline iodide (ChI), as redox active component for the positive electrode. Importantly, this electrolyte is liquid above ~40°C, as identified by differential scanning calorimetry. It shows only glass transition upon cooling, which reappears during heating and is followed by cold crystallization and melting. The hybrid EC in aqueous ChNO3-ChI exhibits a capacitance of 81 F g⁻¹ at 24°C and still 50 F g⁻¹ at ~40°C. The energy and power performance of the proposed hybrid EC and an EDLC made of the same carbon electrodes in organic electrolyte is comparable in the temperature range from 24°C to ~40°C.

4:30 PM ES09.03.03 2D MXenes as Building Blocks for Fabrication of Highly Stable Pseudocapacitive Electrodes Amin VahidMohammadi and Majid Beidaghi; Auburn University, Auburn, AL, USA; Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

High performance carbonaceous materials have been investigated in a wide range of applications, especially in energy storage and water purification. The ability of MXenes to spontaneously intercalate a variety of cations and/or large organic molecules has created the platform for efficient storage or removal of guest species. Fast redox reactions at the transition metal-oxide/hydroxide-like surfaces with efficient charge transfer due to high electronic conductivity, makes MXenes a promising candidate as high rate pseudocapacitive materials for energy storage applications. Furthermore, combination of slit-like pores with electronic conductivity, qualifies MXenes as capacitive deionization (CDI) electrodes for efficient and reversible removal of ionic species. However, an important cornerstone in the development of capacitors using relatively diluted aqueous solutions is the rapid fading of performance when lowering temperature. In this presentation, we show that inorganic MXenes undergo charge transport via hopping of charged species between metallic centers, which appears as an electrochemical function of 2D transition metal carbides and nitrides, supported by in-situ neutron and Raman spectroscopic studies. Importantly, we demonstrate that this unique electronic behavior can be exploited for high performance CDI at low dilutions and at low temperatures. Moreover, we demonstrate that this electronic behavior highly depends on the materials' hydrogen bonding environment. Thus, we show that highly functional MXenes are able to remove ions from aqueous solutions at a much higher rate, in the presence of common interfering ions. This work paves the way for the development of advanced MXene-based capacitive deionization systems.
Two-dimensional (2D) transition metal carbides (MXenes) are among the most promising electrode materials for pseudocapacitive energy storage. MXenes are particularly of high interest because they can store charge in the bulk of their electrodes through ultrafast intercalation of ions and fast and reversible redox reactions. To date, about 20 different MXenes with a general formula of M\textsubscript{x}M\textsubscript{y}\textsubscript{n}X\textsubscript{m}T\textsubscript{z} (M is a transition metal, X is carbon and/or nitrogen, n=1,2, and 3, and T\textsubscript{z} represents different functional groups present on their surface) are synthesized by selective etching of the A layer atoms (i.e., Al) from MAX phases (i.e., Ti\textsubscript{3}AlC\textsubscript{2}), a large group of layered ternary carbides and nitrides.\(^1\) However, from all the available MXene compositions, so far only pseudocapacitive behavior of few MXenes, such as Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, has been systematically studied and pseudocapacitive properties of most other MXene compositions have remained unexplored. The main reason that has hindered such investigations is instability and rapid structural degradation of delaminated (2D) form of other MXene compositions such as V\textsubscript{2}CT\textsubscript{y}. Here we demonstrate the fabrication of highly stable freestanding films of 2D vanadium carbide (V\textsubscript{2}CT\textsubscript{y}) MXene with superior pseudocapacitive properties. We show that a variety of cations including Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, and Al\textsuperscript{3+} can electrochemically intercalate fabricated V\textsubscript{2}CT\textsubscript{y} in aqueous electrolytes, offering capacitances of over 1300 F cm\textsuperscript{-2}. Supercapacitors fabricated using V\textsubscript{2}CT\textsubscript{y} MXene films can deliver gravimetric capacitances of over 200 F g\textsuperscript{-1} at a high rate of 100 A g\textsuperscript{-1} with a cyclic stability of over hundreds of thousands of cycles, surpassing previously reported Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} supercapacitors. Our research describes a new approach for the design and synthesis of high performance layered electrode materials using 2D MXene building blocks.

References


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**ES09.04.01**  
Metastable Charge Activity in Carbon-Based Electrodes for Capacitive Deionization  
Bei Li and Steven T. Boles; The Hong Kong Polytechnic University, Hong Kong, China.

Limitations of capacitive deionization (CDI) technology and future commercialization efforts are intrinsically bound to electrode stability. In this work, the metastable behavior of salt ions and their link to stability degradation is explored. Chemical extraction studies suggest that once mobile species can become metastably trapped in the surface of aged electrodes. To qualitatively explore their impact on CDI devices, a two-electrode voltage sweep test is presented which can simultaneously monitor the active voltage window for CDI between the electrodes without the need for cell disassembly or alteration of the aqueous input feed. This voltage sweep test can be employed in conjunction with long-term operation of CDI cells. Furthermore, annealing treatments in different ambient conditions can assist to gain insights into the nature of carbon-based electrode materials and the formation of different functional groups. Preliminary investigations suggest different behavior in the anode and cathode of the CDI during continuous operation and offer insights into strategies for minimizing electrode degradation as the technology gains momentum for future commercialization.

**ES09.04.02**  
Improving Desalination Performance of Capacitive Deionization Using Novel Operating Schemes—Use of Sinusoidal Voltage and Resonant Operation  
Ashwin Ramachandran\(^1\), Steven A. Hawks\(^2\), Michael Stadtmann\(^3\) and Juan G. Santiago\(^4\); Stanford University, Stanford, California, United States; \(^1\)Lawrence Livermore National Laboratory, Livermore, California, United States.

Capacitive deionization (CDI) performance metrics can vary widely with operating methods. To date, nearly all CDI control schemes have consisted of constant current or constant voltage operation with a constant flowrate. Such operating methods typically show benefits in either energy or salt removal performance, but not both.

In this work, first, we develop a theory around and experimentally demonstrate new operation modes for CDI which use sinusoidal forcing voltage (or sinusoidal current). We use a dynamic system modeling approach and quantify the frequency response (amplitude and phase) of CDI effluent concentration. Using a wide range of operating conditions, we show that CDI can be approximately modeled as a linear time invariant system. We validated this model with experiments and showed that a sinusoidal voltage operation can simultaneously achieve high salt removal and good energy performance. We explore the coupling between electric charge, ionic charge, and mass transport (advection) and demonstrate that sinusoidal voltage forcing functions can achieve resonance-type operation for CDI. Despite the complexities of the system, we find we can describe the resonance mode with the following simple relation: The resonance period (frequency) is proportional (inversely proportional) to the geometric mean of the flow residence time and the electrical resistance-capacitance (RC) charging time. Operation at resonance results in an optimal balance between absolute amount of salt removed (in moles) and avoidance of dilution of the feed and brine streams. The result is a maximum average concentration reduction for the desalinated water. We further developed our model to generalize the resonant frequency operation, and study and compare with the responses to square and triangular voltage waveforms as two examples. To this end, we developed a general tool that uses Fourier analysis to construct CDI effluent dynamics for arbitrary input waveforms. Using this tool, we show that most of the salt removal (~95%) for square and triangular voltage forcing waveforms is achieved by the fundamental Fourier (sinusoidal) mode. We show that the frequency content of the higher Fourier modes severely limit their flow efficiency. Hence, such high frequency modes consume additional energy while providing minimal additional salt removed. This deficiency of higher frequency modes further highlights the advantage of DC-offset sinusoidal forcing for CDI operation.

**ES09.04.03**  
Bifunctional Cathode Configurations in Rechargeable Zn–Air Cells  
Christopher N. Chervin, Jesse S. Ko, Brandon J. Hopkins, Joseph F. Parker, Jeffrey W. Long and Debra R. Rolison; US Naval Research Laboratory, Washington, District of Columbia, United States.

Rechargeable zinc-air batteries are desirable next-generation power sources that promise to deliver high energy density (upwards of 400 Wh kg\textsuperscript{-1}) using aqueous (nonflammmable) electrolytes. We have recently addressed a long-standing problem of dendrite formation at the anode by fabricating the Zn as a 3D sponge. We now turn to another great challenge: the development of an efficient, stable, and practical air cathode that can pair with our Zn anode to deliver extended cycle life and achieve specific energies that surpass today’s Li-ion batteries. Cathode efficiency and stability are determined by the electrode architecture (e.g., porosity, hydrophobicity/hydrophilicity, and electronic & ionic transport) and to a greater extent by the incorporation of high-performance electrocatalysts that can reduce molecular oxygen (ORR) during battery discharge and evolve O\textsubscript{2} via water splitting (OER) upon charging. Our approach is to synthesize ORR and OER electrocatalysts as high surface–area aerogels and then use conventional gas diffusion–electrode fabrication techniques to incorporate these oxide nanoparticles within practical carbon architectures. We choose catalyst compositions that are highly active but only contain earthy abundant elements; namely, cryptomelane (α-MnO\textsubscript{2}) for ORR and nickel ferrite (Ni\textsubscript{Fe}\textsubscript{O}, O\textsubscript{3}) for OER or nickel ferrite alone as a bifunctional OER and ORR catalyst. We assemble Zn-air cells that comprise our Zn sponge anode and aerogel-functionalized composite cathodes and test their cycle stability and ability to deliver practical energy density and power. We will describe results for a series of cathode configurations in which we vary the placement of the ORR and OER catalyst layers and compare cathodes containing a single bifunctional catalyst with those that are made from separate OER and ORR catalysts.

**ES09.04.04**  
Graphene Oxide/Cobalt-Based Nanohybrid Electrodes for Robust Hydrogen Generation  
Fabiola Navarro-Pardo\(^1\), \(^2\), Haiguang Zhao\(^3\), Zhiming M. Wang\(^2\) and Federico Rossetti\(^1\); \(^1\)Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China; \(^2\)Centre for Energy, Materials and Telecommunications, Institut national de la recherche scientifique, Varennes, Quebec, Canada; \(^3\)College of Physics and The Cultivation Base for State Key Laboratory, Qingdao University, Qingdao, China.

Generating hydrogen (H\textsubscript{2}) using photoelectrochemical (PEC) cells is a promising route towards combining a renewable source of energy with the production of a solar fuel. In this
context, considerable advances have been achieved in PEC cells based on semiconductor chalcogenides such as quantum dots (QDs). Within such devices, while QD-based photoanodes have been widely studied, the study of electrocatalysts deposited at the counter-electrode for this type of systems has been overlooked. As such, a major challenge is the development of effective electrocatalysts that possess long-term stability in strong alkaline conditions.

Several efforts have focused on identifying substitutes to enable a H2 economy without the need of Platinum, which is often considered to be the best electrocatalyst in alkaline medium and yet is rare and expensive. Different transition metals have been shown to perform adequately as state-of-the-art earth-abundant inorganic electrocatalysts. In particular, cobalt-based compounds such as cobalt oxides and cobalt chalcogenides are promising electrocatalysts for hydrogenation, due to their low energy barrier for H atom adsorption. These cobalt-based compounds have been mostly studied in alkaline conditions using a KOH aqueous electrolyte. Until now, there are no studies of their performance in a Na2S/Na2SO3 aqueous medium, which is a requirement for effective and stable operation of photocatalytic and PEC systems based in semiconductor chalcogenides.

Here we report the fabrication of cobalt-based nanohybrids (CoNHs) by directly electrospinning CoOx nanoribbons onto large-area carbon fiber paper and demonstrated their application as binder-free electrodes for solar-driven H2 generation. First, we demonstrate that the addition of graphene oxide (GO) can enhance the charge transfer and robustness of the electrode. The addition of 12wt% GO within the CoOx, can lower by ~100 mV the overpotential needed to obtain a current density (J) of ~10 mA cm−2, compared to pristine CoOx. This is corroborated by the reduced charge transfer resistance from 4.4 Ω to 2.5 Ω for p/CoNHs and the optimized GO/CoNHs, respectively. In addition, the CoNHs display outstanding electrochemical long-term stability, as the overpotential required to keep J = ~10 mA cm−2 was invariant for over 42 h. Subsequently, we show that the initial electrocatalyst nanoribbons composed of Co3O4(particles (~10 nm in size) can transform and regenerate in situ into nanosheets, leading to the formation of a mixture of cobalt sulfides (CoS/CoS2), which stabilizes the performance of these electrodes.

Finally, as proof of concept we implemented these CoNHs as counter-electrode in a QD-based PEC device using a CdSe/CdS:TiO2 photoanode in the presence of Na2S/Na2SO3 alkaline media to demonstrate the viability of these electrodes for stable H2 generation. Additionally, we confirmed the versatility of the CoNH electrodes when used as both anode and cathode and connected to a photovoltaic cell to assist solar-driven water splitting in the presence of KOH aqueous electrolyte. Our observations indicate that the GO/CoNH electrode represents a very promising application in renewable energy devices, such as PEC water splitting, electrolysis, and QD-sensitized solar cells.

ES09.04.07
Assessment and Characterization of Hybrid Mesoporous Material MCM with Titanium Dioxide for Water Treatment Jiajun Xu; Mechanical Engineering, University of the District of Columbia, Washington, District of Columbia, United States.

In the current study, a new method was developed to synthesize the hybrid mesoporous material with metallic oxides, MCM-48 with TiO2, at an improved efficiency and reduced cost. The results have shown an over 95% adsorption efficiency for trace metals for the hybrid MCM-48 with TiO2 materials, and a significantly improved maximum adsorption capacity compared to pure MCM-48. Its unique hybrid structured allows the polluted water to pass through the strong yet highly permeable structure of mesoporous material, while gives enough time for the pollutants to react with the TiO2 infused on the porous structure so that the polluted water can be treated without introducing secondary pollutants. The microstructures of the MCM-48 with and without TiO2 are characterized using SEM with EDS and Porosimeter. The effectiveness of wastewater treatment is measured using Inductively Couple Plasma-Mass Spectrometer (ICP-MS). The significant improvements observed here is likely due to the infused TiO2 to the base MCM-48 structure, which also agree with the authors' previous finding. It is noticed that, while the higher concentration of TiO2 has a positive impact on the adsorption of trace metals, the higher concentration of Ti source does not necessarily yield significantly higher concentration of TiO2 in the final product. Future study is needed to further explore this hybrid mesoporous material for other pollutants treatment, and to obtain a further understanding of its mechanisms.

ES09.04.08
Safe, Low-Cost and Sustainable High Concentrated Aqueous Sodium Battery Myeong Hwan Lee, Sung Joo Kim and Kisuk Kang; Seoul National University, Seoul, Korea (the Republic of).

Highly concentrated aqueous batteries have outperformed conventional electrolytes by forming the solid-electrolyte interphase (SEI) layer with anion decomposition and suppressing water activity, thereby expanding the electrochemical stability window. These newly proposed concentrated electrolyte systems enable high-voltage operation of aqueous batteries for a wide selection of electrodes; however, significant economic concerns have delayed the commercialization of aqueous systems, especially regarding the use of expensive inorganic salts. In the current study, we revisited all the commonly used low-cost inorganic salts and evaluated them for their use in super-concentrated aqueous electrolytes. These super-concentrated electrolytes offer a high electrochemical stability window of up to 2.7 V through suppressing water decomposition with forming a super stable SEI layer without involving the reduction of salt anions. The SEI layer exhibited the extraordinary electrochemical storage stability of the full-cell for over 890 hours. Using this new class of super-concentrated electrolyte, we successfully developed a 2-V Na-ion battery with remarkable cycle stability and a coulombic efficiency of over 99% at 1C for over 200 cycles.

ES09.04.09
Polyelectrolyte Modified Nanoporous Membranes for Selective Ion Transport in Electrodialysis Stephen Percival, Sara Russo, Ryan Hill, Amanda Peretti, Leo J. Small, Susan Rempe and Erik D. Spoerke; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Ion selective nanoporous membranes are an important component for the purification of water using electrodialysis. Electrodialysis uses an applied DC electric field to actively transport dissolved ions through the membranes, purifying the water on one side of the membrane and concentrating the salt ions on the other side. This process uses a large amount of electrical energy and thus only finds limited application. In order to increase the efficiency of this process the the ionic selectivity and the ionic conductivity of the membranes must be increased. Our goal is to increase these properties of commercial nanoporous membranes by coated with an inexpensive polyelectrolyte thin films using an aqueous Layer-by-Layer (LBL) process. The polyelectrolyte coating changes the surface chemistry of the membranes leading to changes in the selectivity and conductivity. We can further tailor the properties of the membranes using various crosslinking chemistries to impact not only the chemical selectivity and conductivity but also the chemical stability of the polyelectrolyte surface modification. Polyelectrolyte film structure, such as film thickness, is shown to change the ionic selectivity of the membranes. Additionally, the addition of small functional molecules to the LBL deposition solutions will incorporate the molecules into the resulting thin film. These small molecules, upon crosslinking of the polyelectrolyte, lead to an increase in selectivity. Variations in structure and the composition of the polyelectrolyte film, polyelectrolyte deposition parameters and crosslinking chemistries are shown to controllably influence the ionic selectivity and conductivity of the nanoporous membranes as well as adhesion of the polyelectrolyte coating. Continued advances of these polyelectrolyte thin films will enable the widespread use of electrodialysis as an economical water purification technology.


ES09.04.10
Hydrophilic Carbon Nanotube-Based Thin-film Composite Membranes for Forward Osmosis Application Hsin Hua Lee, Chi-Young Lee and Nyan-Hwa Tai; Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan.

Growing population, increasing water demand and rising energy use over the past few decades stimulated exploration of alternative water and energy resources [1]. For obtaining clean water from seawater by a most energy efficient method, this work proposes the fabrication of carbon nanotube-based membranes and study their application of the membranes on the forward osmosis (FO). Unlike reverse osmosis (RO), FO is an osmotically driven membrane process which can be operated without high hydraulic pressure, thus it has many potential advantages such as low energy consumption and low fouling tendency. Thin-film composite (TFC)-FO membrane separation technology can also be used in many applications, including water desalination, wastewater treatment, food processing and power generation [2]. However, most of the porous substrates for TFC-FO membranes which were made of polymer via the phase inversion method cannot withstand harsh conditions such as strongly acidic, alkaline and organic solutions. In this study, a novel carbon nanotube-based TFC (CNT-TFC) membrane with high hydrophilicity is developed, which possesses high chemical stability, thermal stability and great FO performance. These properties significantly increase the potential of application of the FO membranes in extreme conditions. Besides, the process for the CNT-TFC membrane could be easily scaled up.

The CNT-TFC membrane consists of a hydrophilic supporting layer and an ultrathin active layer. The supporting layer, designated as PET-PDA-CNT, is made of a layer containing polydopamine (PDA)-coated CNTs cast onto a polyethylene terephthalate (PET) nonwoven fabric, and the thickness of the PDA-coated CNT layer is only around 3 μm.
The active layer is an ultrathin polyamide (PA) film synthesized by interfacial polymerization (IP) of 1,3,5-benzenetricarbonyl chloride (TMC) in hexane solution and m-phenylenediamine (MPD) with sodium dodecyl sulfate (SDS) in aqueous phase. To improve the hydrophilicity of the supporting layers, PDA thin films synthesized via self-polymerization are coated on the CNT surfaces. Compared with the pristine PET-CNT supporting layer, the contact angle of the PET-PDA-CNT supporting layer drastically decreases from 77.5° (for PET-CNT) to 34.9°. Owing to the great hydrophilicity and thin thickness, the water resistance of the support layer is decreased and the overall membrane permeability is increased. On the other hand, the addition of SDS, an anionic surfactant, as co-solvent in aqueous phase during the IP process reduces the surface tension between two phases. As a result, it forms a looser PA layer than those synthesized by the conventional IP process. The looser PA layer could result in higher water flux and effectively block the reverse solute.

The results show that the TFC membrane with PET-PDA-CNT supporting layer exhibits great FO performance with the water flux of 12.58 Lm⁻²h⁻¹ and the reverse salt flux of 5.26 gm⁻²h⁻¹ when the selective layer is oriented towards the deionized water feed solution using 1 M NaCl solution as draw solution. The water flux of the membrane with PET-PDA-CNT layer is 267% higher than that of the membrane without the selective layer. The swelling extent of the PDA-CNT layer is 37% lower than that of the membrane with the pristine PET-CNT layer. Besides, it is found that the CNT-TFC membrane fabricated using 0.1 wt% SDS in the aqueous phase during IP could lead higher water flux while maintaining low reverse salt flux.

Nitrate is a common contaminant in groundwater which is a by-product of agricultural activities. Nitrate is, for example, implicated in so-called blue-baby disease. Thus, a point-of-use, reusable device to selective remove ions is crucial. Ionic exchange resins are the predominant method to selective adsorb ionic pollutants. However, the regeneration of these resins requires the disposal of significant volumes of chemicals.

Capacitive deionization (CDI) is a promising technique for water desalination. In contrast to ionic exchange resins, CDI requires no chemical to regenerate. CDI relies on electrical charges for adsorption and regeneration onto high surface area activated carbon (AC) electrodes. However, the experimental and theoretical framework for selective removal of ions with CDI is still under development.

In this work, we explored a method to enhance selectivity with a functionalized CDI system. We functionalized active carbon electrodes with ion-selective functional groups. This functionalization combines the high selectivity advantage of ionic exchange resins with the electrostatic regeneration of CDI. The active electrode was functionalized with cetyl trimethylammonium bromide (CTAB). This cationic surfactant has a quaternary ammonium moiety which acts as a nitrate selective functional group. The counter electrode was functionalized with the anionic surfactant sodium dodecylbenzenesulfonate (SDBS). In this system, the adsorption step occurs at 0 V due to the presence of chemical charge, while the regeneration step occurs at a constant (applied) voltage. We also expanded our understanding of the selective electro-adsorption process by developing and validating a well-mixed reactor model. Our model combines a Donnan treatment for electric double layers (EDL) and electrosorption Langmuir-type equilibria.

The experimental set-up consisted of a cell with a radial architecture. A mixture of sodium nitrate and sodium chloride entered the axisymmetric cell stack from the outer periphery. After treatment, the water exited the cell through a channel along the axis to minimize dispersion. We used ion chromatography to measure the concentration of each ion. We measured the intrinsic selectivity (~7.7) of our CTAB functionalized electrode with an ex-situ experiment. We defined and measured cycle selectivity of nitrate versus chloride as a function of the inlet nitrate concentration and regeneration voltage. We observed that cycle selectivity increases with lower values of voltage, with a maximum of ~6.5 at 0.4 V. We compared and validated our multi-species dynamic model with our quasi-steady state experimental data.

In brief, functionalization of AC electrodes provides a selective ion capture system with that can be regenerated with applied voltage. We demonstrated a nitrate-specific functionalization with up to 6.5-fold cycle selectivity. We also validated a dynamic model which incorporates a Donnan treatment for EDL and Langmuir-type equilibria for surface chemistry.


References

ES09.04.12 Theory and Experimental Validation of Selective Removal of Nitrate Using Capacitive Deionization with Surface Functionalization Diego I. Oyarzun, Ali Hemmatifar, Michael Stademann, Juan G. Santiago, Mechanical Engineering, Stanford University, Stanford, California, United States; Mechanical Engineering, University of Maryland, College Park, Maryland, United States; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, California, United States; Lawrence Livermore National Laboratory, Livermore, California, United States.

Faster and energy-efficient condensation of water vapor contained in atmospheric air has emerged as a solution to the demand for water in some regions of the planet. In these deserts or isolated areas the only accessible source of water is atmospheric air. In this way, academic and industrial research works that seeks to develop water collection devices with high efficiency has great relevance for the scientific community. It’s known that droplets coalescence on nanostructured superhydrophobic surfaces may result in droplet jumping from the surface. It can happen due to the release of excess surface energy because the surface roughness is much smaller than the coalesced drop size. In this work, we aim to show that if designed properly the modified carbon nanotubes forest can block the condensed drop at micrometric length scales during condensation easier than the hydrophobic, hydrophilic and superhydrophilic surfaces. In addition, this behavior occurs, for our surface, at high super saturation level which is an innovative aspect of this work. The Vertically Aligned Carbon Nanotubes were grown on stainless steel pipes. We used a CO2 laser and a O2 plasma to perform the post treatments that changed the nanotubes to superhydrophobic and superhydrophilic, respectively. In addition, the CO2 laser treatment added a second level of roughness in the surface by etching the walls of the nanotubes. Due the low adhesion of the carbon nanotubes with the substrate a Polyethylene layer was deposed on carbon nanotubes avoiding the removal of them. We experimentally demonstrated a 30% higher vapor condensation rate at high supersaturations levels in comparison to the others prepared surfaces.
In this work a V-O cell achieves total efficiency between 42 and 62% depending on the current density and stable operation was demonstrated during extended tests.

The “dual circuit redox flow battery” takes advantage of a conventional all-vanadium redox flow battery (VRFB) combined with a catalytic hydrogen evolution reactor in a separate external circuit. Depending on demand, the VRFB can be conventionally discharged by an electrical load or by using the catalytic reactor to yield $\text{H}_2$.

The dual-circuit vanadium redox flow battery coupled with a catalytic reactor, water is oxidized to oxygen and $\text{VO}_2^{2+}$ does not possess a potential high enough to spontaneously drive the oxygen evolution reaction; an additional energy input is required. Thus, in this work the reaction is performed electrochemically in a secondary flow cell (V-O$_2$ cell) to provide a high rate of conversion while minimizing the energy required. In the V-O$_2$ electrolyzer, which was added to the VRFB with catalytic reactor, water is oxidized to oxygen and $\text{VO}_2^{2+}$ is reduced to $\text{VO}^{3+}$ electrochemically providing state-of-charge and proton rebalancing for the dual-circuit redox flow battery system.

The main advantage of this approach is that there are no additional chemical species. Water oxidation reaction proceeds with the support of a stable and commercially available DSA® electrode. Moreover, from a practical point of view the V-O$_2$ cell, being actively driven by current can be switched on and off asynchronously with the hydrogen production in the catalytic reactor. Also, in principle, this system can guarantee much higher hydrogen and oxygen purity than a typical electrolyzer, because of the physical, local, and temporal separation on the production of the two gasses. In this work a V-O$_2$ cell is proposed and optimized according to its energy input and a final prototype which integrates a catalytic reactor, a VRFB, and the V-O$_2$ electrolyzer is successfully tested. A laboratory scale cell was investigated in a complete dual-circuit system including a V-O$_2$ cell. The dual-circuit vanadium redox flow battery coupled with a V-O$_2$ cell achieves total efficiency between 42 and 62% depending on the current density and stable operation was demonstrated during extended tests.

Capacitive deionization (CDI) is an emerging water desalination technology accomplished by electrosorption of ions at the interface between saline solutions and nanoporous carbon electrodes. By employing the strictly physical process of ion electrosorption, salt adsorption capacities of typically 15-20 mg/g (mg salt per g of the electrode) have been reported. The use of carbon limits the maximum achievable charge storage capacity and restricts the applicability of CDI to low molar media (typically below 20-50 mM). This issue originates from unfavorable co-ion expulsion from carbon nanopores concurrently occurring during counter-ion adsorption. Only once all co-ions have become depleted in the pores, permselective ion removal is accomplished. To transfer CDI from a niche technology to a more largescale use, new electrode materials and cell concepts need to be explored.

The use of ion intercalation or conversion reaction electrodes has recently re-energized the research field for electrochemical water desalination. The presentation will summarize key aspects of the implementation of ion intercalation materials for the desalination of aqueous media with ion concentration levels typical brackish water and seawater. We demonstrate the facile use of pseudocapacitive materials to effectively remove cations and anions from saline media. Such materials, like transition metal carbides (MXene), some transition metal dichalcogenides (e.g., MoS$_2$), or some metal oxides (e.g., V$_2$O$_5$) allow energy efficient desalination in the absence of an ion exchange membrane. These benefits also can be accessed using electrode materials with battery-like charge/discharge behavior, such as TiS$_2$. With enhanced ion mobility and lowered energetic barriers, there is even an improved desalination performance when increasing the salt concentration from low (10 mM) to high levels (1 M). The adaptation of intercalation materials requires careful considerations for the desalination cell design.
The rising demand of clean & safe drinking water is one of the primary concerns because of the water scarcity, growth of human population, urbanization, & natural & anthropogenic pollution. Ground water & surface water resources are being contaminated by pervasive low molecular weight hydrophilic compounds (LMHcs) which are not effectively removed by current water treatment technologies. The US Environmental Protection Agency (USEPA) is focused on the removal of many classes of LMHcs from drinking water & wastewater, including; disinfection byproducts precursors, pharmaceuticals, personal care products, heavy metals & perfluoralkylated substances (PFAs). These LMHcs, especially PFAS, do not hydrolyze or degrade in water. Some of these have been reviewed to have adverse health effects while for others the long term exposure effects are still unknown. In order to address removal of these pervasive contaminants, an anion exchange resin polymer (AEP) functionalized Single Walled Carbon Nanotubes (SWCNTs) in the form of NanoResin has been developed. The large surface area of SWCNTs increases the availability of active ion exchange sites of the AEP. These NanoResins have higher & faster adsorption capacity compared to currently commercialized materials like magnetic ion exchange resins, DOWEX, etc.

This NanoResin was synthesized by modified activator regenerated electron transfer atom transfer radical polymerization technique in all aqueous media where the growing hydrophilic polymer brushes get attached the surface of hydrophobic SWCNTs. The hydrodynamic diameters of the purified AEP & NanoResins measured using dynamic light scattering were 1.660 ± 0.10 nm & 194.9 ± 11.3 nm, respectively. The ratio between D & G bands, measured using Raman Spectroscopy, increased by 100% compared to pristine carbon nanotubes which is indication of covalent functionalization of the AEP. The proton nuclear magnetic resonance of the growing AEP showed 33 % conversion from monomer to polymer in 40 minutes. The scanning electron microscopy of nanoresin films fabricated on mixed ester cellulose membrane for performance testing showed a smooth morphology of mesoporous architecture of SWCNTs with conformal polymer coating. The step height of fabricated film (0.046 mg-NanoResin/cm²) measured under atomic force microscopy was 142.31 nm. The measured membrane resistance of the thickest nanoresin film (0.184 mg-NanoResin/cm²) was determined to be R = 2.11x10¹¹ m⁻¹ which is smaller than typical ultrafiltration membranes with R = 2x10² m⁻¹ and hence, demonstrated its high water flux capacity.

We demonstrated the removal of several types of pharmaceuticals (viz., tetracycline hydrochloride and carbencillin disodium), pesticides (viz., bentazon, terbacil, and bromacil), DPBs (viz., bromocetic acid and chlorocetic acid) and PFAS (viz., perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS)), from water via adsorption capacity measurements. The percentage removal of PFOA and PFOS, for a starting concentration between 2-4 mg/L of contaminant, was 92.7% and 95.8%, respectively. Since, the US EPA has been challenging systems to measure ~95% removal of PFAS at low concentrations, we established adsorption of PFAS at a starting concentration of 3-5 μg/L and removed PFAS upto ~98%. The regeneration studies performed upto 20 cycles, showed a slope of -0.23 ± 0.18% per cycle which demonstrates that the NanoResin could be regenerated without significant degradation. Recently, we have been employing sonochemistry to synthesize Aq-SNR to be more consistent with the principles of green chemistry.

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We later show is a signature of electron-conduction limitations in PBA NP agglomerates. Galvanostatic cycling of electrodes with different average NP-agglomerate sizes reveals that two-fold higher rate capability is achievable when agglomerate radius reduces two-fold, despite having the same NP size distribution. By way of comparison with theory and by characterizing the effective conductivity of PBA-NP compacts, we show that apparent cation diffusion in PBAs is limited by electronic conduction through NP agglomerates. Building on these findings we also measure the effective electronic and ionic conductivity and hydraulic permeability of porous electrodes incorporating non-conductive nanoparticles from which we build process/structure/property relationships to inform materials selection for desalination devices using cation intercalation materials. We subsequently identify optimal electrode formulations by introducing electrochemical Ashby diagrams with guidelines determined using device-level metrics for electrochemical desalination.

The continual increase in global population, along with a rapid progression towards extensive urbanization and industrialization, serves as the driving force for the upsurge in the development of water desalination technologies. There are only a limited number of ion removal technologies available on the market. Distillation is used for ion streams with high salt concentration, reverse osmosis (RO) is used for both intermediate salt concentrations as well as brackish water, and electrochemical technologies like electrodialysis (ED/EDR) and capacitive deionization (CDI) are used for brackish water with relatively low salt concentrations. In addition to desalination, there is an increasing demand for the selective uptake of ions. Along this line of motivation, CDI has the potential to offer diverse means to accomplish selective ion separation from aqueous solutions.

CDI is a water desalination technology that facilitates adsorption of ions via two oppositely polarized porous electrodes. In a traditional sense, CDI typically utilizes high surface area carbon materials, where the ions are trapped within the electrical double layers (EDLs) formed in the pores of the carbon electrodes [1]. However, in recent times, new hybrid carbon-intercalation electrodes employing materials with redox activity have been introduced to CDI [2, 3], in which the ionic species are stored in the crystallographic sites of the intercalation host compound (IHC).
Preferential ion electrosorption in capacitive deionization (CDI) has been the primary focal point of a number of contemporary studies. In general, the major influential factors that regulate ion selectivity of these porous electrodes include: (i) operating conditions such as applied cell voltage and initial ion concentration, (ii) ion properties like ion valence, hydrated size, and electronegativity, and (iii) micropore characteristics such as chemical surface groups and pore sizes. Hence, the technological hurdles associated with the development of efficient CDI electrodes with enhanced ion selectivity are manifold. Furthermore, a comprehensive knowledge of the underlying mechanisms and the materials involved is of prime importance to enact successful optimization of relevant process parameters (e.g., voltage, current, flow, cycle time), to attain preferable ion selectivity during the adsorption/regeneration phase.

This talk will be centered on the comparative analysis between conventional CDI electrodes with porous carbons, and the most recent intercalation electrodes [4, 5-6], utilized for the purpose of water desalination and selective ion separations. In the case of the latter, redox-active nickel hexacyanoferrate (NiHCF) nanoparticles embedded in a carbon matrix facilitates the intercalation and de-intercalation of Na+ ions, producing fresh water via a cyclic charging and discharging CDI process. Conclusively, alternate materials that can offer potential in advancing ion separation process will be also discussed.

This presentation provides a general overview addressing various material challenges in relation to ion removal within the domain of CDI.

References:
difficult to achieve both high conductivity and high selectivity simultaneously. We have synthesized a series of ion conducting membranes incorporating a novel physical crosslinking mechanism that appear to have significantly increased conductivity with little to no decrease in counter-ion selectivity, compared to covalently-crosslinked membranes. Physical crosslinking also enhances the mechanical properties of the membranes by increasing their ductility. The observed behavior cannot be rationalized via the conventional understanding of the conductivity-selectivity tradeoff, which is based on membrane swelling and its effect on Donnan exclusion. As such, our results suggest that our understanding of the physicochemical factors governing ion sorption and transport in charged membranes is incomplete. In this presentation, we propose an additional physicochemical mechanism to explain our findings and discuss its implications for design and optimization of ion-conducting membranes.

8:45 PM ES09.08.04
Layered Manganese Oxides as Intercalation Electrodes for Water Desalination via Hybrid Capacitive Deionization Ekaterina Pomerantseva; Drexel University, Philadelphia, Pennsylvania, United States.

With increase in the world population and climate change, the importance of and demand for the water desalination systems continue to grow. Liquid surface freshwater constitutes only ~0.5% of the water available on Earth, and thus, desalination of brackish and saline water is becoming increasingly important as the water crisis escalates. An emerging method, hybrid capacitive deionization (HCDI), is a derivative of capacitive deionization (CDI) approach for water desalination, in which one carbon electrode is replaced with a redox-active intercalation electrode, resulting in substantial improvements in ion removal capacity over traditional CDI. However in order to keep pace with rising levels of water consumption, the performance of HCDI systems needs to be improved while maintaining low cost and minimizing environmental impact. As a result, novel scalable and cost-efficient materials that exhibit superior performance are sought for.

In this study, two crystallographically and chemically distinct layered manganese oxides (LMOs), Na-birnessite and Mg-buserite, were investigated as intercalation electrodes for HCDI. The layers in crystal structures of LMOs consist of edge sharing MnO₆ octahedra, while Na⁺ and Mg²⁺ ions, known as stabilizing ions, occupy the interlayer positions in the Na-birnessite and Mg-buserite, respectively, along with water molecules. The large difference in interlayer spacing of Na-birnessite (7.2 Å) and Mg-buserite (9.7 Å) is attributed to the different amount of structural water residing between the layers: one layer of water in Na-birnessite compared to two layers of water in Mg-buserite. To understand the ion removal performance of these two materials, Na-birnessite and Mg-buserite electrodes were cycled in NaCl and MgCl₂ solutions in an electrochemical cell with the HCDI configuration. The chosen electrode materials and solutions provide a platform to investigate ion dynamics when stabilizing ions in the electrode structure and ions in solution are the same and when they are different. To gain insights into the stability of layered manganese oxides as HCDI electrodes, the cells were stopped after both 200th ion adsorption step (IAS) and ion release step (IRS), followed by post-mortem analysis of the electrode materials structure and composition. Replacing carbon electrode after 200 cycles with a fresh one, allows us to evaluate the contributions of capacity decay related to the structural changes in layered manganese oxides and oxidation of carbon electrodes. Both materials demonstrated excellent initial ion removal performance with the highest capacities of 37.2 mg/g (637 μmol/g) exhibited by Mg-buserite in NaCl solution and 50.2 mg/g (527 μmol/g) exhibited by Na-birnessite in MgCl₂ solution. The performance decay observed over the course of 200 ion adsorption/ion release cycles was attributed to two major phenomena: oxidation of carbon electrode and evolution of the structure/composition of LMO electrodes. The latter involves disorder in stacking of Mn-O layers and changes in the interlayer spacing/interlayer ions reflecting the composition of the solution being desalinated. This work highlights the importance of understanding the interactions between the HCDI electrodes and solutions containing different ions and the structural analysis of redox active materials in intercalation electrodes over the course of operation for gaining insight into the fundamental processes governing desalination performance and developing next-generation HCDI systems with long-term electrochemical stability.

The rate of phase change between the homogeneous mixture and the separated IL/water biphasic mixture upon heating or cooling should be rapid but may require facilitation via proper engineering. An example of LCST ILs continuous flow FO reactor will be presented and discussed. This scheme could radically reduce the energy-intensity of water purification.

Acknowledgments

This work was supported by funding from the Assistant Secretary for Energy Efficiency and Renewable Energy, Geothermal Technologies Office of the US Department of Energy under the USDOE contract number DEAC02-05CH12311 for Lawrence Berkeley National Laboratory. Work conducted at Idaho National Laboratories was performed under Contract No. DE-AC07-05ID14517. J.F.D. acknowledges the support of Dr. Kevin Wilson and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division of the U.S. Department of Energy.

9:30 AM ES09.09.03

Capacitive Deionization—Leveraging the Electric Double Layer for Selective Water Desalination  Eric Guyes, Tahel Malka and Matthew Suss; Technion Israel Inst of Technology, Haifa, Israel.

Capacitive deionization (CDI) is a fast-emerging water desalination technology, most often applied to brackish water desalination and water softening.[1,2] CDI cells desalt feedwaters by storing ions in electric double layers within micropores of electrically charged carbon electrodes. CDI cells have demonstrated a size-based ion selectivity wherein smaller ions are preferentially electroabsorbed over larger ions due to ion volume exclusion interactions.[3] Selective ion removal is a highly desirable feature in water treatment systems, as selectivity mechanisms can be leveraged towards preferential and energy efficient removal of toxins and other undesirable ions. We here demonstrate that the size-based selectivity exhibited by microporous CDI electrodes can be substantially boosted through addition of chemical charge to micropores via surface functionalization.[4] We develop a theory of size-based ion storage in micropores including the effect of chemical charge,[5] which predicts such enhancements and demonstrates they are a result of enhanced counterion crowding in functionalized micropores. Desalting an electrolyte consisting of competing potassium and lithium ions, we demonstrate that a surface functionalized (oxidized) cathode increases the selective removal of the smaller potassium ion. We observe that the largest enhancements are measured at lower cell voltages, for example from a selectivity factor of ~1 for typical electrodes to 1.8 for surface functionalized electrodes at 0.4 V charging voltage. This counter-intuitive result is demonstrated to be due to significant cathode chemical surface charge degradation occurring at higher cell voltages, a phenomenon which has not been previously reported upon in the CDI literature to our knowledge. Model results show that achieving stabilized surface groups at high electrode potentials can lead to further enhancements in size-based selectivity factors achievable by CDI electrodes

References


9:45 AM ES09.09.04 Enhanced Tunable Ion Selectivity in Flow-Through Electrode Capacitive Deionization with Advanced Carbon Aerogel Electrodes  Patrick G. Campbell, Steven A. Hawks, Maira R. Ceron, Jennifer Knipe, Tuan Anh Pham and Michael Stadermann; Lawrence Livermore National Lab, Livermore, California, United States.

The selective removal of toxic or otherwise undesirable water has the potential to dramatically reduce the cost of water treatment. Capacitive deionization (CDI) removes ions from solution using charged electrodes and has demonstrated significant energy savings compared with reverse osmosis for removal of salt from low salinity or brackish water. By tailoring electrode properties such as pore morphology and surface functionality, as well as cell operating parameters, selective separation of ions can be achieved. Lawrence Livermore National Laboratory’s unique flow-through electrode CDI platform has demonstrated remarkable selectivity for removal of toxic nitrate in the presence of chloride and sulfate ions, as well as tunable preferential absorbance of monovalent over divalent cations based on electrode material properties. In this talk, we will present our latest results including the development of a multi-scale model (FE + QMD) to help elucidate the mechanism(s) for ion selectivity in CDI.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Document release number: LLNL-ABS-760441

10:00 AM BREAK

SESSION ES09.10: Water-Energy Nexus II

Session Chairs: Ekaterina Pomerantseva and Matthew Suss

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 131 A

10:30 AM *ES09.10.01 Water Technologies by Interface Engineering Seth B. Darling1,2,3, Ruben Waldman2,1,3, Hao-Cheng Yang4, Edward Barry4, Subramanian Sankaranarayanan4 and Jeffry Elam1,2; Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois, United States; 3Advanced Materials for Energy-Water Systems (AMEWS) Center, Argonne National Laboratory, Lemont, Illinois, United States; 4Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois, United States; 5Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, United States; 6Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

Driven by climate change, population growth, development, urbanization, and other factors, water crises represent the greatest global risk in the coming decades. Advances in materials represent a powerful tool to address many of these challenges. Understanding—and ultimately controlling—interfaces between materials and water are pivotal.1 In this presentation, we will lay out the challenges and present several examples of work based on materials science strategies for addressing applications in water. In each instance, manipulation of interface properties using either atomic layer deposition (ALD) or sequential infiltration synthesis (SIS) provides novel functionality, ranging from selective transport to energy transduction to pollution mitigation.


11:00 AM *ES09.10.02 Anion-Based Redox Pseudocapacitance of the Perovskite Library La1−xSrxB03−δ (B = Fe, Mn, Co) Keith Stevenson2 and Caleb Alexander1;1University of Texas at Austin, Austin, Texas, United States; 2Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, Russian Federation.

This presentation will describe the synthesis of a library of perovskite oxides with the composition La1−xSrxB03−δ (x = 0-1; B[KJP1] = Fe, Mn, Co) to systematically study anion-based pseudocapacitance. The electrochemical capacitance of these materials was evaluated by cyclic voltammetry and galvanostatic charging/discharging in 1 M KOH with the highest specific capacitance of 492 F g−1 at 5 mV s−1 for La0.5Sr0.5MnO3−δ. We find that greater oxygen vacancy content (δ) caused by systematic incorporation of Sr2+ increases the surface-normalized pseudocapacitance for the three B-site transition metal series investigated, but the slope of the trends is controlled by the B-site element.
Furthermore, the first all-perovskite asymmetric pseudocapacitor has been successfully constructed and characterized in neutral to alkaline aqueous electrolytes with a maximum voltage window of 2.0 V in 1 M KOH. An asymmetric, perovskite pseudocapacitor’s cell voltage can be increased by increasing the voltage difference between the perovskites’ different transition metal redox potentials in the B-site. Asymmetric capacitors constructed from SrCoO$_2$-$x$, La$_{0.8}$Sr$_{0.2}$MnO$_3$, and BM-Sr$_2$Fe$_2$O$_5$/SrCoO$_2$$_7$ combination performing the best with a high energy density of 31 Wh kg$^{-1}$ at 450 W kg$^{-1}$ and power density of 10,000 W kg$^{-1}$ at 28 Wh kg$^{-1}$.

11:30 AM ES09.10.03

The Flow Efficiency Limits Capacitive Deionization Performance for Relevant Separations

Steven A. Hawks$^1$, Patrick G. Campbell$^2$, Ashwin Ramachandran$^3$, Juan G. Santiago$^1$ and Michael Stadtmann$^1$; Lawrence Livermore National Laboratory, Livermore, California, United States; $^1$Department of Aeronautics & Astronautics, Stanford University, Palo Alto, California, United States; $^2$Department of Mechanical Engineering, Stanford University, Palo Alto, California, United States.

The flow efficiency is an underappreciated loss mechanism inherent to cyclic capacitive deionization (CDI) operation. This efficiency factor ultimately limits performance and desalination depth when approaching industrially-relevant separations. The flow efficiency parameter is defined to reflect the fact that desalinated water inside a cell is partially lost to re-salination if desorption is carried out immediately after adsorption. This efficiency is distinct from, and yet multiplicative with, other highly-studied current efficiencies. Flow efficiency losses can be minimized by flowing more feed solution through the cell; however, this also results in less efficient concentration reduction due to mixing with the feed.

We show that the flow efficiency concept is a key tool for identifying loss processes occurring during desalination, understanding the performance of different operation modes, and recognizing the key scaling factors that underlie the operational response.

11:45 AM ES09.10.04

Atmospheric Water Harvesting with Composite AQSOA Zeolite Layers

Alina LaPotin$^1$, Sameer Rao$^2$, Hyunho Kim$^2$ and Evelyn Wang$^1$; Mechanical Engineering, The University of Utah, Salt Lake City, Utah, United States; $^1$Korea Institute of Science and Technology, Seoul, Korea (the Republic of k); $^2$Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Atmospheric water harvesting has received recent interest owing to the abundance of water in the atmosphere. This approach is distinct from state-of-the-art dewing approaches because it can efficiently operate in extreme conditions, that is at low relative humidity and temperature. When the moisture content of air is low, AQSOA zeolites (Z01 and 202) are aluminophosphate-based microporous molecular sieves that are stable in water and have been extensively studied for adsorption-based refrigeration. Their pore filling mechanism, i.e., Type IV or V isotherm behavior, leads to a sharp uptake at a low relative humidity (5-15% RH) which is indicative of uniform micropore size and a relatively low adsorption enthalpy. In addition, the adsorption enthalpy and the temperature required to desorb the water vapor is lower compared to other zeolites (e.g., 65 degrees C for AQSOA Z01). In this work, we characterized AQSOA zeolites for water harvesting. One challenge of using solid adsorbents is the relatively slow vapor transport via diffusion in the bulk material. The vapor transport occurs at two length scales: through the bulk material (intercrystalline) and to the pores within an individual crystal (intracrystalline). In a practical device, the intracrystalline transport resistance of AQSOA zeolites can have a significant influence on the kinetics because it occurs over a length scale roughly three orders of magnitude larger than the intracrystalline vapor transport. Transport resistance is also highly dependent on the packing porosity of the adsorbent, which can inhibit mass transfer at high packing densities. Therefore, we fabricated composite adsorbent layers using AQSOA zeolites and metal foam to facilitate both heat and vapor transport. To study the mass transfer characteristics of AQSOA zeolites in this composite layer, we performed adsorption, desorption, and vapor condensation under controlled pressure and temperature. We compared our experimental results to our detailed computational models which capture the diffusive processes at these different length scales. Our results indicate the promise of using composite AQSOA zeolite layers, and can be extended to design other composite adsorbent materials for water harvesting.


1:30 PM *ES09.11.01

Turning a Cheap, Poor Catalyst into a Cheap, Excellent Catalyst—Optimizing Layered MnO-Based Materials for Water Oxidation Using Experiment and Theory


Efficient catalytic water oxidation is an important milestone for the development of solar hydrogen as a source of green energy. Extraction of high energy electrons from water for the preparation of fuel leaves O$_2$ as a byproduct. Nature boasts the only truly effective catalyst for this reaction, the oxygen evolving complex (OEC), a tetramanganese-calcium-oxygen-oxo cluster. The exploration of solid-state manganese oxides inspired by (or possibly a primordial precursor to) this inorganic cluster is of interest for the chemical and electrochemical oxidation of water, and while promising catalysts have been discovered, an understanding of their active sites structures and mechanisms has been elusive, precluding incremental improvements in design. This lecture is focused on the bimimsette phase of MnO$_2$, typically viewed as a poor water oxidation catalyst. The Center for Complex Materials at Temple University is undertaking a combined experimental and theoretical approach where Density Functional Theoretical (DFT), and Molecular Dynamics (MD) computations inform and guide experimental approaches as to understand the functioning of, and thereby identify ways to improve the catalytic activity of these materials. Modification of bimimsette by enrichment with Mn(III) defect sites, intercalated interlayer Co or Ni ions, and alloying of the layers with Co(III) has turned this relatively poor catalyst into one competitive with excellent IrO$_2$, cobalt-oxide-, and double-layer-hydroxide-based catalysts. The discoveries have been guided by MD simulations which show enhanced geometric frustration of water enhances electron transfer rates, and DFT calculations which describe geometric features that optimize band structure for beneficial electronic conductivity and charge separation.

2:00 PM *ES09.11.02

Amorphous Photocatalysts for Photocatalytic Solar-to-Chemical Production

Candace K. Chan; Arizona State Univ, Tempe, Arizona, United States.

In the last decade, remarkable efforts have been devoted to the development of novel approaches and materials to convert solar energy directly into storable fuels and other chemicals. One approach to achieving lower cost, more sustainable photocatalysts is to use amorphous materials. Since high temperature treatments for crystallization are not required, amorphous materials can be potentially much cheaper to synthesize and easier to adapt for large-scale preparation. However, for efficient solar energy conversion, it has been commonly accepted that highly crystalline materials are required for effective electron-hole pair generation and separation. In photocatalytic systems, photogenerated carriers must diffuse to the electrolyte interface to catalyze redox reactions at the surface of the photocatalyst; hence, avoiding recombination at defects in the bulk is important. On the other hand, several recent studies have shown that amorphous or disordered materials can display higher photocatalytic activity than crystalline counterparts, particularly in high surface area and unstructured, and/or mesoporous materials. This can be explained by the fact that small nanoparticles or mesoporous materials have a small bulk volume and large accessibility to the electrolyte. This means that photogenerated carriers only have to diffuse a short distance before they can reach the electrolyte interface where the catalytic reactions occur.

In this work, amorphous titania-based photocatalysts are synthesized using a facile, UV-light mediated method and evaluated as photocatalysts for hydrogen evolution and nitrogen
reduction to ammonia. The photocatalysts are prepared through the direct injection of a titanium alkoxide precursor into a water/methanol mixture, with subsequent hydrolysis, condensation, and polycondensation to form TiO2(OH)x species under UV-irradiation. The resulting amorphous titania materials exhibit an overall higher hydrogen evolution rate compared to a crystalline TiO2 reference (P25) due to the highly porous structure and high surface area (~500 m²/g). Synchrotron pair distribution function data show that the short-range local structure of the freshly synthesized materials is brookite-like, but that ageing and re-crystallization to anatase occurs after storage in ambient conditions.

Under photocatalytic reaction conditions, the formation of surface Ti³⁺ species in the amorphous photocatalyst was observed, as indicated by the deep blue coloration of the materials, is thought to play an important role on the chemical reactivity of the catalyst. The Ti³⁺ species are also used to reduce protons to H₂ in the absence of light irradiation or reduce Pt²⁺ to form Pt nanoparticles. The results show that this is a facile approach for the preparation of high surface area titania photocatalysts containing Ti³⁺ species with good photocatalytic activity and unique porous morphology to overcome the limitations presented by increased likelihood of charge carrier recombination in amorphous materials.

2:30 PM ESO9.11.03
Biomimetic Carbon Nanotube Water Treatment Systems Utilizing Electro-Dynamic Interfaces
Bruce Hinds; University of Washington, Seattle, Washington, United States.

An important challenge for the membrane community is to mimic natural protein channels that outperform, by orders of magnitude, man-made systems based on pore size and coarse chemical selectivity. To mimic protein channel pumping on a robust engineering membrane platforms, applied bias can be used to actuate charged gatekeepers and induce ionic pumping. Carbon nanotubes have three key attributes that make them of great interest for novel membrane applications 1) atomically flat graphene surface allows for ideal fluid slip boundary conditions and extremely fast flow rates 1,2 2) the cutting process to open CNTs inherently places functional chemistry at CNT core entrance for chemical selectivity and 3) CNT are electrically conductive allowing for electrochemical reactions and application of electric fields gradients at CNT tips. The CNT membrane, with tips functionalized with charged molecules, is a nearly ideal platform to induce electro-osmotic flow with high charge density at pore entrance and a nearly frictionless surface for the propagation of plug flow 3,4. Use of the electro-osmotic phenomenon for responsive/programmed transdermal drug delivery devices for nicotine addiction [5]. Electrophotois and electroosmosis phenomena are discussed in detail through CNT conduits. Another approach is to mimic natural protein channel transport cycles with binding/transit/release/reset events. Porous alumina (AAO) membranes have top and bottom electrodes coated with thin Au layers with pore dimension tuned to match protein dimensions. At this thin layer at pore entrances, Ni-NTA is able to bind to hystag residue on target protein, as is commonly employed in chromatography. A binding voltage pulse attracts anionic target protein to top electrode and blocking the pore, while repelling the cationic imidazole release agent. The second voltage cycle attracts cationic release agent to top of membrane while pumping anionic target protein to bottom permeate and resetting the pumping cycle. The separation efficiency of 1cm² of membrane was comparable to conventional 1cm² volumes used in chromatography [6]. Further modeling of system kinetics shows order of magnitude increase in throughput with sub-second cycle times enabled with high imidazole concentrations in a continuous cross flow operation.


2:45 PM ESO9.11.04
Direct Solar Absorption Nanoparticle-Doped Membranes for a Hybrid Membrane Distillation/Photovoltaic Cell
Alejandro Espejo, Drake Norman and Todd Otanicar; Mechanical Engineering, The University of Tulsa, Tulsa, Oklahoma, United States.

The growing demand for clean water supplies is driving the need for an innovative approach of water desalination. Developing a method for treating water with high salinities is possible with membrane distillation (MD). Additionally, MD is very attractive for pairing with solar energy due to the low temperature requirements which integrate well with solar thermal. Integration of a membrane distillation system with a photovoltaic (PV) system will result in the co-production of electricity and clean distillate; and therefore, improve the economics of MD. Such a hybrid system will directly absorb thermal energy in the membrane for desalination while taking advantage of the spectrally selective nature of PV to generate electricity. At the top of the system is a PV cell that will filter the visible light wavelengths and transmit the remaining ultraviolet and infrared to a membrane doped with absorbing nanoparticles located at the core of the system. This provides the means to integrate this system but also provides an avenue for increasing the temperature polarization coefficient and improving the membrane performance. The proposed membranes will be fabricated using a multi-step phase inversion approach that will allow for controlled distribution of nanoparticles across the membrane. The model developed here can be used to systematically evaluate the hybrid design where heat is provided from PV cell waste heat and selective transmission and absorption directly into the membrane. The overall project would lead to increased use of renewable energy for desalination while improving the ability to use MD for desalination purposes. Additionally, the spectral optical properties of the membranes and potential PV cell materials are integrated into the model for realistic device performance predictions.

3:00 PM BREAK

SESSION ESO9.12: Water-Energy Nexus III
Session Chairs: Ekaterina Pomerantseva and Michael Zdilla
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 131 A

3:30 PM *ES09.12.01
The Promise and Challenges of Implementing Insertion and Phase Change Compounds in Electrochemical Deionization Devices
Jay E. Whitting,1; and Meagan Mauter1,2; 1Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 2Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 3Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Insertion compound materials, which can attract significantly higher volumetric ion concentrations compared to high surface area activated carbons commonly used for CDI, are appealing and still underexplored. These materials posses stable redox potentials that can be leveraged to avoid electrolysis losses and commensurate pH shifts, and can have excellent long-term stability depending on operational conditions. They are also inherently ionically selective in that insertion compound will attract some species and reject others during electrochemical biasing. In this talk, we seek to comprehensively address benefits and challenges of using insertion compounds for CDI in different water concentrations, pH values, and compositions. Specifically, our presentation will explore (a) the origins of electrolysis and other losses in CDI systems and how insertion compounds might be used to overcome these issues, (b) the behavior of two different compound materials in solutions with a wide range of concentrations and compositions, and (c) comparative assessment of deionization devices that used static vs. slurry flow electrodes. Multiple insertion and phase change compounds will be discussed, and their performance in salt concentrations ranging from 10 to 1000 ppm will be discussed using half cell and full CDI device – level data. Results suggest that while better voltage control and volumetric ion densities are possible, overpotential losses and transport asymmetry issues can be problematic, particularly in solutions of lower concentration. The ability for insertion compounds to selectively remove one ionic species over another will also be addressed and contextualized.
In response to compounding challenges to global water-energy systems, researchers are investigating advanced membrane structures to reduce the energy costs associated with separations and fluid manipulations. Janus membranes are an emerging class of separation materials in which the two sides of a membrane are engineered to have opposing properties. Examples of such properties include wettability, surface charge, and catalytic activity. Janus membranes have been studied for oil/water separations, ionic rectification, and efficient water aeration. The Janus property interface’s placement within the membrane is critically important in dictating how the membrane behaves. However, many fabrication methods rely on interfacial reactions that are highly sensitive to processing conditions and offer limited control of the property interface position. A method for fabricating Janus membranes providing tunable control of the property interface position would enable optimization of the Janus structures for advanced fluid manipulations.

We have used atomic layer deposition (ALD) of hydrophilic Al2O3 to achieve Janus membranes on hydrophobic polypropylene (PP) ultrafiltration membranes.1 While ALD is normally considered a conformal material growth technique, two factors in the PP membrane system cause a gradient deposit to form. The trimethylaluminum precursor used to grow Al2O3 has a low sticking probability on PP, and the mean free path of the precursor vapor molecules far exceeded the pore path lengths in the tortuous high-aspect-ratio PP membrane. The combination of PP membrane poor surface chemistry for ALD nucleation and physical dimensions that yield Knudsen flow, coupled with physical masking that limited vapor exposure to one membrane face, are what allowed for Janus membrane fabrication. ALD processing parameters including the number of cycles, duration of each vapor exposure, and purge time between co-reactant vapors, were found to influence the resulting gradient of Al2O3 coverage within the membrane interior. Using energy-dispersive x-ray spectroscopy (EDS) on the membranes prepared in cross-section, the concentration profiles of aluminum as a function of depth in the membrane were measured. These data demonstrated clear control over the shape and position of the concentration profile.

The ALD-derived Janus membranes were used in an anion experiment. The membranes were secured supporting a column of water above pressurized air. Air coated the hydrophobic surface of the untreated PP membranes and was released as large bubbles. In contrast, the hydrophilic surface of the PP membranes was poorly wet by the emerging air bubbles. This served to reduce the adhesion force between the air and the membrane surface, allowing buoyancy to release the bubbles at a much smaller size at the same air flow rate for rapid gas diffusion into the water. These ALD-derived Janus membranes offer a platform for study on the role of gradient wettability interfaces in novel fluid manipulations. Applying this technique to other materials such as TiO2 may introduce catalytic activity as an additional functionality.

References:

4:15 PM ES09.12.03
Mechanisms of Aqueous Charge Storage and Degradation in Manganese-Rich P2 Oxides

Shelby Boyd1, Natalie R. Geise2, James B. Mitchell3, Rohan Dhall1, James M. LeBeau1, Michael F. Toney2 and Veronica Augustyn1; 1North Carolina State University, Raleigh, North Carolina, United States; 2Stanford University, Stanford, California, United States.

Transition metal oxides are of interest as aqueous intercalation materials in neutral-pH electrolytes for alkali ion batteries and redox-active desalination because of their high capacity and ion intercalation potentials, but few possess high stability in aqueous electrolytes. Understanding the behavior of transition metal oxides, particularly the more stable manganese-based oxides, could enable the design of high capacity, safe, and long-life aqueous electrochemical energy storage. The P2 layered Na3 manganese-rich oxides widely studied in non-aqueous electrolytes have higher theoretical capacities and voltages for Na intercalation than other manganese-based oxides. While they have previously been shown to be redox active in aqueous electrolytes, this work presents the first systematic study of the factors controlling the interlayer chemistry and redox behavior of these P2 materials in aqueous electrolytes. We show the intertwined effects of applied potential and composition on the interlayer chemistry and redox activity of P2 oxides by investigating compositions previously shown to exhibit a range of moisture stability: Na1.82Mn2.86Fe0.12O2 (NaFeMn), Na1.82Mn2.86Co0.12O2 (NaCoMn), Na1.82Mn2.86Cu0.12O2 (NaCuMn), and Na1.82Mn2.85Cu0.15O2 (NaCuMg). When cycled beyond a critical Na content, all compositions experience an irreversible loss of Na in the first anodic cycle and subsequently intercalate water to form a brinesite-like phase. The composition determines the potential at which this critical Na content occurs, with the Cu substituted materials exhibiting greater retention of the P2 phase. The behavior in aqueous electrolytes is characterized using in situ transmission electron microscopy and X-ray diffraction (XRD) to understand the structural effects of the presence of water, and in situ synchrotron XRD to understand the phase transformation accompanying the intercalation of water. In addition, the effect of electrolyte water concentration on the intercalation behavior and potential window is studied using water-in-salt electrolytes. Overall, these results present a study of the factors that determine the stability and performance of P2 oxides in aqueous electrolytes, and offer guidance for designing transition metal oxides compatible with aqueous electrolytes.

4:30 PM ES09.12.04
Atom Probe Tomography as an Emerging Characterization Technique for Materials Applications to the Water-Energy Nexus

Ingrid McCarroll1, Daniel Haley2, Paul Bagot3, Michael Woody4 and Julie Cairney1; 1The University of Sydney, Sydney, New South Wales, Australia; 2Materials, The University of Oxford, Oxford, United Kingdom.

Here we will present new tools that allow atomic scale characterization of samples relevant to the water energy nexus, providing valuable information about, for example, nanoconfinement or liquid/solid interface chemistry. Custom adaptations to the local electrode atom probe (LEAP) allow for the transfer of atom probe samples, under ultra-high vacuum and cryogenic temperatures, between a purpose built glovebox, an SEM/FIB with cryo-stage and EBSD/TKD characterization capabilities, and the atom probe analysis chamber. Examples of the capabilities of this new environmentally controlled sample preparation and characterization suite are to be presented for the first time. The current research is focused on the phenomenon of hydrogen trapping within steel samples susceptible to hydrogen embrittlement and the corrosion of magnesium alloys. However, the potential application is much broader and could be used for the study of electrocatalytic reactions. Of particular note is the potential of the current workflow to capture and characterize metal/liquid interfaces.

Atom probe tomography (APT) is a characterization technique recognized for its ability to provide near atomic resolution in three dimensions, providing mass-to-charge-state ratios for each identified ion. A recent adaptation to a local electrode atom probe, at the University of Oxford, enabled vacuum transfer of samples between a catalytic reaction cell and the atom probe analysis chamber. This adaptation has been used to analyze magnesium alloys after controlled gas exposure, without the potential for further reactions to occur within incidental atmospheres encountered during sample transfer. Through this study we were able to observe a correlation between the presence of hydrogen within the magnesium alloys and an increased rate of oxidation. This study highlights the ability of APT to characterize properties such as nanoconfinement and interlayer chemistry, key concerns of the water-energy nexus.

4:45 PM ES09.12.05
Chemical Pre-Intercalation as a Means to Control the Structure and Electrochemical Performance of Layered Oxide Electrode Materials

Mallory Clites and Ekaterina Pomerantseva; Drexel University, Chesapeake Beach, Maryland, United States.

Beyond Li-ion (BLI) alkali ion-based batteries are rising in interest among researchers because of their utilization of more abundant, cost-effective charge carriers, including Na+ and K+. In these systems, compared to traditionally used Li+ ions, however, because such systems utilize electrochemically cycling ions with larger ionic radii, achieving fast diffusion and high insertion rates of the BLI carriers into traditional, close-packed electrode materials is challenging. As such, these new systems require the development of novel electrode materials with high capacity, rapid charge transfer, and stable behavior over extended cycling. Materials with open, layered crystal structures have proven themselves among the most reliable electrode materials for Na-ion and K-ion based systems, exhibiting high performance in these emerging systems. Tuning and control of interlayer spacing and chemical composition in open layered structures, can be accomplished via simple wet chemical modification approaches. Such tailoring has the capability to increase ion mobility and insertion rates as well as enable new redox chemistry. One approach that may lead to improvements in electrochemical performance of these electrode structures. Layered vanadium pentoxide (V2O5) phases are promising cathode materials for BLI systems as vanadium can be present in its highest oxidation state, 5+, and can undergo multiple reductions to a 3+ state, allowing for the transfer of up to two electrons per vanadium ion. One family of vanadium oxide phases that demonstrates advanced electrochemical performance in Li-ion and BLI Na- and K-ion systems is the bilayered δ-M3V2O7 family, where M represents alkali (Li+, Na+, K+) and alkal-earthy (Mg2+ and Ca2+) ions.1-3 The bilayered structure is built from double layers of VO2 polyhedra which are separated by a large interlayer spacing. When no ions are intercalated within this
interlayer spacing, the δ-V\textsubscript{2}O\textsubscript{5} phase exhibits an interlayer spacing of 11.5 Å which is stabilized only by intercalated water molecules. In this non-ion containing structure, capacity typically decays over extended cycling, due to lattice breathing and the gradual breakdown of the lamellar stacking of the V-O layers. Ion-containing δ-M\textsubscript{2}V\textsubscript{5}O\textsubscript{10} phases can be synthesized via chemical pre-intercalation and allow for the tunability of the interlayer spacing from 9.65 to 13.44 Å depending on the nature of the inserted ion.[3] Further, synthesis of the electrode materials via chemical pre-intercalation approach can lead to increased capacities and electrochemical stability in Li-ion, Na-ion, and K-ion cells.

This presentation will focus on the chemical pre-intercalation approach as a means to improve electrochemical performance of bilayered vanadium oxide electrodes in Na- and K-ion systems. Electrochemical performance of δ-M\textsubscript{2}V\textsubscript{5}O\textsubscript{10} (M = Li, Na, K, Mg, Ca) in Li-ion cells will also be presented as a reference. This chemical pre-intercalation technique will be demonstrated to improve electrochemical performance through two modes: (1) pre-intercalation of charge-carrying into the bilayered phase can lead to tailored ion transport and increase overall specific capacities, and (2) pre-intercalation of electrochemically inactive ions to stabilize the bilayered structure and improve capacity retention through BLI ion cycling. While this pre-intercalation may lead to the partial reduction of the oxidation state of vanadium present in the structure, high discharge capacities over 200 mAh/g are observed in all three ion-based systems. A detailed study of the mechanism of charge storage and the effect of charge-carrying ion size on demonstrated capacities and electrochemical stability in Li-ion, Na-ion and K-ion batteries will also be discussed.


SYMPOSIUM ES13

TUTORIAL: Data-Driven Design of Sustainable Materials Process and Products in Early State R&D: Al/Machine learning, Coupled Techno-Economic and Life Cycle Analysis, and Metrics for a Circular Economy
April 22 - April 22, 2019

* Invited Paper

TUTORIAL
Data-Driven Design of Sustainable Materials with Artificial Intelligence, Machine Learning and Assessment
Monday Afternoon, April 22, 2019
PCC North, 100 Level, Room 123

Materials are critical enablers for reducing the resource intensity of society’s industrial, commercial and energy systems. But materials themselves also require resources and can negatively impact humans and the environment, thereby compromising the sustainability of our world. To promote materials development for a more sustainable world, it is essential that the material footprint be better understood and improved for all products and processes. Fundamental research is required that addresses: the creation and sharing of sustainability-related data, metrics and assessments of materials, processes, and performance; use of this knowledge to inform sustainability-focused decision making; improved decision-making tools to enable product and process designers and engineers to incorporate sustainability metrics at the earliest stages of the design phase; and establish better defined sustainability metrics for policy makers. This tutorial brings together leading experts in sustainability who are using machine learning and data-driven design of materials and processes to focus equally on the economic, performance and societal dimensions of sustainability.

This tutorial will introduce approaches and tools for quantifying not only the technological performance impacts of selecting specific materials and processes, but also their economic, environmental, societal, and human health impacts. This approach puts design tools in the hands of materials researchers for creating materials and processes that meet the needs of humanity, not just for today but for future generations.

1:30 PM
Using AI for Sustainable Materials: New Approaches, New Challenges Elsa Olivetti; Massachusetts Institute of Technology

Tutorial will present case examples of the role that AI might play in materials development with an eye towards improving environmental and economic sustainability. These examples will be drawn from academic research as well as industrial cases. Particular focus will be on accounting for the context in which a material operates to understand the appropriateness of particular mitigation strategies. Participants should gain insight into methods to quantify environmental impacts of materials choice on all aspects of the life cycle considering the context in which the material operates and the role that data analytics might play.

2:30 PM BREAK

3:00 PM
Tools for Techno-Economic, Life-Cycle, and Logistics Analyses for Creating Sustainable Materials, Processes and Circular economies Hongyue Jin; The University of Arizona

This tutorial will show the power of using techno-economic, life-cycle, and logistics analysis in assessing the opportunity for early-stage technologies to provide sustainable solutions. Techno-economic analysis (TEA) aims to identify, quantify, and ultimately surmount the technical and financial barriers that hinder the commercialization of new technologies, products, and processes. Life cycle analysis (LCA) identifies the environmental hotspots and pinpoints improvement opportunities that influence consumers, companies, and policy makers in their purchasing behaviors, product design, and policy development decisions. Since the data required for LCA is often a subset of the data required for TEA (or vice versa), an integrated study of TEA and LCA is beneficial as it maximizes the knowledge gained from a given set of information. With TEA and LCA, a better knowledge may be obtained from multiple perspectives. For example, TEA informs us of the potential profit structure of a business, which helps formulate a strategy to maximize the financial gain. By combining the knowledge from TEA and LCA, a problem may be formulated for maximizing the overall economic and environmental benefits. One example of such integrated approach is demonstrated by the optimization of reverse logistics. Operations research techniques are applied to develop mathematical models and derive practical solutions. In this tutorial, several examples will be demonstrated for value recovery of rare earth containing products, using TEA, LCA, and optimization techniques described above.
This tutorial will present two tools – GreenScreen for Safer Chemicals and Chemical Footprint Project – and examples of their application for measuring the chemical footprint of products and organizations. Chemical footprinting is the process of measuring chemicals of high concern in products and supply chains. GreenScreen provides a framework for both identifying chemicals of high concern and safer chemicals. Chemical Footprint Project specifies how to aggregate chemical of high concern data from products to the organizational level. This tutorial will detail examples of how companies and standards use GreenScreen to identify chemicals of high concern and safer chemicals, and how companies use Chemical Footprint Project to calculate their chemical footprint, quantify their baseline use of chemicals, and report reductions in their chemical footprint.

**Quantitative Tools to Advance the Use of Safer Chemicals and Sustainable Materials**

Mark S. Rossi; Clean Production Action

This tutorial will present three tools – GreenScreen for Safer Chemicals and Chemical Footprint Project – and examples of their application for measuring the chemical footprint of materials and products. Chemical footprinting is the process of measuring chemicals of high concern in products and supply chains. GreenScreen provides a framework for both identifying chemicals of high concern and safer chemicals. Chemical Footprint Project specifies how to aggregate chemical of high concern data from products to the organizational level. Plastics Scorecard applies GreenScreen to measure the chemical footprint of plastic materials. This tutorial will detail examples of how companies and standards use GreenScreen to identify chemicals of high concern and safer chemicals, and how companies use Chemical Footprint Project to calculate their chemical footprint, quantify their baseline use of chemicals, and report reductions in their chemical footprint.
Metal recovery from electronic product is currently focused on high-volume metals that are easily recoverable and on low-volume, high-value precious metals. Current and future electronics will increasingly contain small quantities of materials which are not recovered in today’s recycling infrastructure. These materials include rare earth elements that are critical to today’s technology-driven society due to their importance to clean energy as well as the risk associated with their near-monopolistic supply. In this talk, an INEMI (the International Electronics Manufacturing Initiative) project will be discussed on value recovery from hard disk drives that include critical materials. Demonstration projects were completed on direct reuse of entire hard drive, direct reuse of voice coil magnet assemblies, transformation of used rare earth magnets into “new” magnets, and production of rare earth oxide from shredded hard drives. The relevant life cycle inventory data were collected from project participants across industries and national laboratories to perform life cycle assessment. Accordingly, the environmental impacts were quantified for each recovery pathway and were compared with the virgin production impacts. The study also identified the environmental hotspots of each technology, highlighting the future work directions. The ultimate goal of this research is to support closing the material loop, reducing solid waste, and aligning industry with circular economy.

Implementing a Circular Economy results in major changes across product life cycles, including new business models, advanced remanufacturing and recycling processes, but might also involve a change of product designs. On the example of circular design trends of electronics products apparent material trends will be explained. Modularity of products is one such design trend, which is supposed to facilitate reparability, recyclability, and/or upgradeability. However, modularity requires some design changes. In case of mobile communication technology, such as smartphones or tablet computers, the most evident design change is the need for connectors to provide mechanical and electrical contact between individual modules. Depending on the nature and use scenario of a connector reliability, robustness, wear resistance and non-reactive surfaces are required. Gold is the material of choice for such interfaces. In recent years the amount of gold used in electronics decreased, now with emerging modularity among ICT devices gold as a material with a high environmental impact might return into devices in larger amounts. For reversible mechanical fasteners a broader range of technologies might be employed, frequently magnets are proposed as a simple and robust option. To achieve strong magnetic forces rare earth elements are used, mainly neodymium or other critical raw materials, such as cobalt. Rare earth elements are not yet properly recovered from waste electrical and electronic equipment, thus modularity might even contradict better recyclability. The presentation will explain different modularity approaches for smartphones, some of these being already available in the market others are still in a conceptual phase. This variety of modularity approaches is related to different value propositions, thus leading also to a broader range of modularity archetypes. Analyzing technologies for modularity leads to a group of “Modularity Materials”, which are essential for such circular design approaches, but at the same time are among those materials with a large environmental footprint or limited recyclability. Furthermore, some standard materials are likely used more excessively, such as module housing or larger printed circuit boards to accommodate for on-board connectors. A Life Cycle Assessment of a modular smartphone shows a roughly 10% higher environmental life cycle impact compared to a conventional design. This needs to be compensated by reaping the Circular Economy benefits of a modular design, i.e. higher likelihood of getting a broken device repaired, extending the lifetime through hardware upgrades and refurbishment. The Life Cycle Assessment of the Fairphone 2 has shown, that a lifetime extension from 3 to 5 years leads to a significantly lower environmental impact despite the use of “modularity materials”. Consequently modularity is an appropriate approach for a Circular Design, but the user is key for a materialization of the theoretical benefits.

With a detailed view on such correlations the presentation gives a sound overview of trade-offs between different Circular Economy strategies. This research facilitates the understanding of future material trends in smart mobile devices and paves the way to improve the whole product eco-system for lower total environmental impacts.

The research presented in this paper is an outcome of the project sustainablySMART. The project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement no. 680640.

Since new electronic technologies for information and communications and renewable energy are developed at a rapid rate, various materials are significantly used in electronic industry. Among them, rare and precious metals need to be secured for the industry regardless of economic and political situations because they are used as essential materials for the technologies. Also, some metals need to be safely managed in the production, disposal, and recycling stages by preventing their releases to the environment because they are hazardous and toxic to human health and ecosystems. Since newly developed technology affects the contents of metals contained in electronic products, technology development itself can positively or negatively affect potential environmental impacts of products. Thus, this study assesses environmental effects of technology development to figure out whether advanced electronic technology is desirable and what metals are to be managed with priority to prevent environmental impacts. Five case studies are carried out to demonstrate the various environmental effects of technology developments: (i) technology evolution of smart phone; (ii) technology transformations from liquid-crystal display (LCD) to organic light emitting diode (OLED) display, hard-disk drive (HDD) to solid-state drive (SSD), and polycrystalline silicon to amorphous silicon and copper/indium/gallium/di-selenite (CIGS) solar photovoltaics (PVs); and (iii) technology convergence to tablet PC. The resource depletion, hazardous waste, and toxicity potentials of the respective technologies are assessed based on the mass and concentrations of metals contained in the samples of the representative electronic products and environmental impact characterization factors used in life cycle impact assessment methods. The results of this study shows that all the technology developments do not contribute to reducing the environmental impact potentials and that the priority heavy metals are different depending on the technology. Therefore, environmental impacts assessments on advanced technology are required to inform manufacturers to reduce the priority materials and potential environmental impacts of advanced technology-based products in the product design stage and recyclers to safely recover and manage rare, precious, and toxic materials in the end-of-life stage for sustainable circular economy.
Additive manufacturing (AM) is beginning to enter commercial manufacturing, but its environmental impacts can often be larger than traditional mass manufacturing. Many inventors are developing new "green" materials for 3D printing, but almost none have measured their benefits, and no government agencies have set targets for desired impacts. This study establishes a protocol by which to quantify environmental and functional properties of AM materials, to guide the industry towards developing more sustainable materials and processes.

Previous studies show that AM's environmental impacts are dominated by the energy used during printing, but alternative materials can radically decrease AM energy demand. Instead of necessitating high temperatures to melt thermoplastics, materials that bond or harden chemically at ambient temperature can reduce printing energy use, while also reducing other environmental impacts such as resource depletion, toxicity, and waste. In order to identify viable green alternatives that meet industry performance standards and provide gains in sustainability, this comprehensive protocol combines three environmental metrics into one overall sustainability score and combines three market viability metrics into one overall functionality score. Together, these can be used to aid decision-making, benchmarking, and goal-setting, to drive the industry toward more sustainable production.

Based on the National Academy of Sciences (NAS) method for chemical alternatives assessment, this protocol is customized for relevance to AM. The three environmental metrics are whole-system life cycle assessment (LCA), toxicity, and resource circularity. The LCA integrates seventeen ecological impacts into a unified score using the ReCiPe methodology, and measures not only material production, but the whole printing system, including printing energy, printer embodied impacts, and end of life. Resource circularity is calculated using the Cradle to Cradle Nutrient Reutilization formula. Toxicity is measured using an enhanced version of GreenScreen, using its eighteen hazard categories but providing additional precision and displaying uncertainties (quite common in hazard data). The three functionality metrics are mechanical performance, cost, and expert print quality evaluation. Mechanical performance is measured by a combination of ultimate strength and modulus of elasticity, comparing to ABS plastic's properties. Cost includes only the cost of materials, not saved printing energy costs, because the latter are usually small. Print quality is measured by industry experts handling physical samples and quantitatively rating them on a Likert scale while adding qualitative comments.

Once environmental and functional scores are determined, new alternative materials can be compared to other AM materials, such as ABS and PLA plastics, and can be evaluated on their fitness for a variety of AM applications. This should help inventors of new materials quantify their benefits; it should also help set benchmarks of current best practices and targets for future goals. Together, these metrics and goals can drive the additive manufacturing industry toward a future that is not more damaging, but more sustainable than current production.

Additive manufacturing methods have great potential for rapid production of parts and devices in remote areas with limited access to supply chains. This work examines the use of mineral resources for inexpensive and low-energy additive manufacturing. In particular, Earth abundant minerals in conjunction with polymeric binders such as polyethylene glycol (PEG) were used as the material base to print structural components. Silicate, basaltic, and other refractory minerals were chemically functionalized and incorporated in tandem with binders in fused filament fabrication (FFF) or in paste printing. Filaments with powder loading up to 50 vol.% were achieved and used in a commercial FFF printer to fabricate structures, while higher loading was achieved in printing similar structures using commercial paste printers without compromise in structural and mechanical integrity. This work paves way for efficient in situ resource utilization in hostile environments.

Additive manufacturing and 3D printing are synonymous with rapid prototyping and production in limited quantities of or more complex parts and design. Can 3D printing be an important component of a more circular economy? Will it replace traditional high throughput manufacturing? What are the materials challenges for the Six-R concept? Polymers and metals are the materials of primary interest for materials sustainability. An important aspect of 3D printing is distributed production and digital manufacturing that can cross traditional blockchain supply models and distribution. This talk will outline and review important developments and the value chain of 3D printing towards the following: 1) Challenges of adopting the right 3D printing methods and the intricate relationship with the starting material and desired part properties, 2) Savings in time, cost and reduction of waste materials in 3D printing by materials design, 3) Unique applications of 3D printing and replacement of traditional manufacturing modes towards high performance and limited production, and lastly 4) Bio-inspired and design paradigms towards high strength and lightweight materials from aeropace to biomaterials. The talks will also highlight our work employing fused deposition modeling (FDM), selective laser sintering (SLS), and stereolithographic apparatus (SLA) or photopolymerized fabrication of nanocomposite materials. Lastly, the importance of designing polymer materials for the six-R can be emphasized in the early stages of new materials and process development.

Additive for Clays as a Sustainable Alternative in Construction

The construction is a sector that consumes a significant part in the environmental impact throughout the life cycle. Along with the infrastructure, consume on average half of the materials extracted from the earth's crust. Likewise, it adds millions of tons of CO2 poured into the atmosphere each year, accelerating the greenhouse effect and global warming. With this situation, many efforts begin to be notable, innovations and inventions are made every day in order to reduce the degradation of the environment. One of the most promising paths is the use of sustainable materials in the building, among which clay stands out for its characteristics, such as disposal, reintegration into the environment and low energy cost. The present article presents the results of laboratory tests of clay mixed with an additive of natural components for the most part, which improves the resistance of the clay to compression, as well as the drying time, which allows its hardening without the need of high temperatures. The text also suggests that clay with additive can be used in the construction of building elements such as bricks, in molds or extruder methods.

Approaches to the Development of Environmentally Friendly and Resource-Saving Technology for Solar-Grade Silicon Production

Currently, the main material for the production of solar cells is still silicon. More than 70% of global production of solar cells is silicon based. For solar-grade silicon production the technologies based on the reduction of silicon from organosilicon compounds are mainly used. These technologies are energy-consuming, highly explosive and unsustainable. The paper presents the comparison results of a new chlorine-free solar-grade silicon production technology based on purification of metallurgical-grade silicon by vacuum-thermal
methods with the existing technologies. The proposed technology provides environmental safety, energy consumption reduction, the process scalability and the cost reduction of obtained silicon.

In this paper, the following studies have been carried out—technical processes of vacuum-thermal and plasma-chemical purification of metallurgical-grade silicon under the conditions of electromagnetic stirring of silicon melt by the mathematical modeling; comparison study of the existing technologies for the production of solar-grade silicon and the investigated technology as far as material consumption, energy intensity of the processes concerned.

The research results are—the results of the study of a new chlorine-free technology for solar-grade silicon production are shown; a comparison study of the existing solar-grade silicon production technologies and the investigated technology is performed; it is shown that the use of the proposed technology reduces the cost, material consumption and energy intensity of the process.

ES13.02.02 Structural, Optical and Electrical Properties of Transparent Conducting Oxide Based Thin-Film Transistors Kelsey Yarbrough, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, Norfolk, Virginia, United States.

In the past few years, intensive studies on oxide thin film transistors (TFTs) have been reported for their widely use in driving active matrix organic light emitting diodes (OLEDs). Zinc oxide (ZnO) has been the primitive material that is widely used to fabricate TFTs due to its good optical and electrical properties, good uniformity, and low process temperature. Among various ZnO-based TFTs, one of the most promising materials is indium gallium zinc oxide (IGZO), which shows high electron mobility. However, IGZO thin film requires high film deposition and annealing temperature as well. Similarly, indium element is a rare element, and the storage of indium in the form of ore is very limited on earth. The indium-free oxide-based channel materials such as tin doped zinc oxide (TZO) thin film deposited on glass substrate have been optimized using physical deposition technique and their structural, optical and electrical properties have been extensively studied. Sn is a non-toxic, abundant on earth, and it is reported to possess excellent electrical and optical characteristics. This work focuses on TZO thin film performances grown by Pulsed Laser deposition on n-type silicon and glass at different temperatures to analyze the effect of growth morphology. The effect of Sn content on microstructures, surface morphology and optoelectronic properties of the films were investigated by X-ray diffraction, Atomic Force Microscopy (AFM), Field Emission-Scanning Electron Microscopy (FE-SEM), Ultra-violet visible spectroscopy, and electrical characteristics. AFM provided thin film roughness, grain size, and surface morphology for both glass and silicon substrates. FE-SEM was used to show the surface morphology with change in deposition time and temperature. The present work will provide valuable scientific input of TZO thin films for the improvement of TFT devices.

ES13.03.03 Establishment of a Tea-Waste Recycling System Based on the Concept of Chamu Pin Gao, Kyushu University, Fukuoka, Japan.

Tea produces a large amount of waste during the production process, and the current use of such tea waste does not fully exploit its value. This study reprocessed tea waste to create a new kind of biodegradable material dubbed CHAMU, and, based on the Six-R processes, the concept of a tea-waste recycling system was proposed. In studying this concept, the composition and characteristics of tea waste were analyzed through a literature review. Tea waste is classified into fiber and non-fiber elements, and the different kinds of waste should be processed in different ways. In a molding experiment, the fiber waste was subjected to hot pressing and injection-molding, while the non-fiber waste was subjected to an injection-molding experiment. A universal testing machine (UTM) was used to test the mechanical strength of the CHAMU material, and the biodegradability of the material was examined using the soil-burial test method. These experiments established the practicality of the tea-waste recycling system. The article concludes by describing how the CHAMU material was redesigned to make a series of CHAMU products, and, using the method of design and perceptual analysis, discusses the potential of the high-value-added recycling of tea waste based on this system.

ES13.03.04 Thermomechanical Design Optimization for Low Metal Footprint in Hybrid Metal-Polymer Heat Exchanger Manjushri C. Rajagopal, Ho Chen Cheng, Yuquan Meng, Gowtham Kantumalla, Timothy Man, Gabriele Balamontte, Shreemath Sundar, Han Yang Zhao, Srinivasa Salapaka, Placid Ferriera, Chunfai Shao, Nemad Miljovic and Sanjiv Sinha; University of Illinois at Urbana-Champaign, Illinois, United States.

Material and maintenance costs of metal-based heat exchangers surpass profits in waste heat recovery (WHR) from ultra-low temperature (<100°C) sources [1]. A low-cost alternative like polymer pipes suffer from poor thermal conductivity (~0.2 W/mK), and a low overall heat transfer coefficient. Polymers’ thermal conductivity have previously been enhanced through systematic molecular alignment by stretching [2], chemical vapor deposition of extended polymers [3], surface grating [4], etc. However, these approaches suffer from scalability issues for WHR heat exchangers in terms of cost [3], and thermomechanical considerations [5]. In this work, we propose novel hybrid metal-polymer heat exchangers that are made from polymer-copper strips. Through finite element method (FEM) simulations, we first optimize the placement of copper around polymer strips to enhance the transverse thermal conductivity of the strips. The copper cladded polymer strips are wound helically in a roll-to-roll system to form the pipes for a heat exchanger. We then optimize the design of helically wound pipes to reduce thermomechanical strains (< 0.2 % at 100°C and 40°C working conditions. At 25 % volume fraction of copper in the pipe, we predict up to 20 % enhancement in overall heat transfer from a base polymer with a thermal conductivity of 0.2 W/mK. We also compare and contrast the thermomechanical performance of the optimized metal-polymer strips to random metal matrix composites. Finally, we experimentally verify the thermal conductivity of the optimized strips through bulk thermal conductivity and thermal interface resistance measurement setup. By systematically improving the design through FEM and experimental measurements, we provide an optimized design of hybrid metal-polymer pipes that provides a low metal footprint and cost-effective means for harvesting waste heat from ultra-low temperature sources.

Recycling is not an objective in itself, but for the benefit it can bring, including reductions in life-cycle costs, energy use and environmental impacts, and dependence on scarce or imported materials. The options available now for recycling of lithium-ion batteries are not optimal, so research and development (R&D) is needed to make economic processes available for use by the time large volumes of batteries from electric vehicles and other uses go out of service. Even if they find a second use, the batteries will eventually be unusable, and the material will need to be recycled. However, by then the material could be a 20 year-old formulation with little residual value from its structure or contained elements. In particular, cathode formulations are evolving towards varied morphologies, emphasizing formulations that contain reduced quantities of cobalt (the valuable element sought in most current recycling operations), reducing the incentive for recycling with standard pyrometallurgical or hydrometallurgical methods.

Several key questions must be addressed by R&D. Most of these are related to the cathode, which is the most valuable form of material that can be recovered. How can the cathode be separated from the other cell components? Can they be recovered as well? How can optimal cathode function get restored? Can we separate one cathode type from another? Can we modify the cathode composition or morphology to update it for reuse? This presentation will describe new research projects to address these questions.

8:30 AM *ES13.04.02
Niobium Technology—Production, Properties and Applications Rogerio M. Ribas1 and Robson d. Monteiro1,2; Catalysis Consultoria Ltd, Rio de Janeiro, Brazil; CBMM, Araxá, Brazil.

Niobium is a Group V element with relatively abundant of 20 ppm in the Earth’s crust. Though it is not rare and its natural occurrence is similar to most of the transition metals, niobium enjoys a limited market demand, of around 52,000 tons in 2016. Major producing countries are Brazil, with the world’s largest proven deposits that account of more than 80% market share of niobium products, and Canada [1]. Niobium chemistry is very rich and versatile owing to its mult-valence states (-1 to +5), which implies in very attractive physical and chemical properties. Niobium oxides and related compounds show a large variety of polymeric structural modifications and metastable phases. These features allow niobium oxides to be extensively used in the preparation of heterogeneous catalysts and of many roles they can play in catalytic formulations are as active phase, solid acids, promoters, supports and redox components. Several industrial applications are found in selective oxidation, acid-catalyzed reactions, biomass conversion and emission control technologies [2]. More recently, the use of niobium has been extended to energy-related materials by exploring its electronic properties into storage and energy conversion devices such as supercapacitors, fuel cells, lithium-ion batteries and electrochromic materials [3]. The purpose of this contribution is to give an account of the current status of the global niobium industry and its supply of niobium products. It will also highlight the most relevant industrial developments of niobium-containing heterogeneous catalysts and energy-related materials.


9:00 AM *ES13.04.03
Integrating Criticality and Sourcing Considerations into Material Selection Decisions Gabrielle Gaustad1, Michele Bustamante2, Alexandra Leader3 and Elsa Olivetti2; 1School of Engineering, Alfred University, Alfred, New York, United States; 2Massachusetts Institute of Technology, Cambridge, New York, United States; 3Rochester Institute of Technology, Rochester, New York, United States.

Critical and strategic materials are characterized by their importance in key applications and their vulnerability to supply chain disruptions. Much current research focuses on identifying and quantifying metrics and indicators that can predict potential supply chain risks for these materials. Sourcing also plays an important role in the environmental impacts of these materials as well. The complexity of both environmental impact and criticality metrics creates challenges to their integration in traditional material selection tools. This work examines the potential for synthesis of these tools in several case study material systems from the clean energy, defense, and electronics industries. This research work uses a functional unit framework borrowed from life-cycle assessment methodologies to quantify metrics for substitution that can better capture functionality trade-offs. It also uses techno-economic analysis to identify material systems where disruptive adoption could cause criticality induced price volatility. Results indicate this approach has several advantages over current qualitative and semi-quantitative indicators and may be better equipped to inform firm-level research and development activities.

9:30 AM *ES13.04.04
Assessing the Environmental Benefits of Materials Recovery in Commodity Materials Elsa Olivetti; Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Environmental benefits attributed to recycling rely on the assumption that we are substituting energy intensive primary production for lower-impact secondary production. However, this argument tends to be a purely engineering lens on a complex socioeconomic system. Research has begun to test whether closing material and product loops does, in fact, prevent primary production. The basis for this counter argument is that when secondary replaces primary, it decreases the price of secondary and thus more primary will switch to secondary if possible, causing primary price to drop, and driving up demand for more primary which may negate the potential for substitution. There is a strong parallel in this argument to the concept of energy efficiency rebound, and is also related to as the potential for secondary material to displace primary production. The critical aspects that influence displacement are the ability of secondary products to substitute for primary products, and price effects. This presentation will describe tools and analytical modeling efforts that explore the potential for recycling displacement for the case of commodity materials such as paper, copper and aluminum. These approaches help to assess the contexts under which recycling may reduce a material or product footprint.

10:00 AM BREAK

10:30 AM *ES13.04.05
Challenges and Opportunities for Sustainable Materials Use and Circular Economies in Photovoltaics and Lithium-Ion Batteries Dustin Mulvaney; Department of Environmental Studies, San Jose State University, San Jose, California, United States.

Photovoltaics coupled with lithium-ion battery storage are widely heralded as a major part of climate and air pollution solutions, and early evidence from sustainability science support these claims. However, reaching terawatt levels of global photovoltaic electricity generation will require innovations, policies, and practices to encourage sustainable materials use. Some photovoltaic technologies rely on significant portions of the overall demand for several key metals for semiconductors suggesting future supplies will need to be augmented by circular economy concepts. By 2045, the total mass of electronic waste from photovoltaics will pass all other e-waste combined, suggesting this could be a major source of future supplies of key materials. Similarly, some of the metals used to make lithium-ion battery have supply chains that are linked to human rights abuses and environmental contamination in developing countries, with some companies announcing intention to recycle key materials or avoid sourcing them in the future. My talk will highlight the motivations for a circular economy, identify the challenges and opportunities to transition away from linear material flows in photovoltaics and lithium-ion batteries, and describe recent trends in sustainability and corporate social responsibility (CSR) in practice in these sectors. Key quantitative key metrics produced by life cycle assessment (LCA) will be presented alongside qualitative evaluations (embodied environmental justice). I will also review emerging standards and frameworks (certifications, supply chain disclosures) used to evaluate, highlight and promote sustainability efforts. My talk will conclude with a critical discussion about the limitations of LCA metrics and CSR information that describe and document the environmental, health, and safety performance of these clean technology manufacturers and their supply chains and suggest how to make LCA, sustainability policy, and CSR efforts generate more actionable information to inform circular economy solutions to enhance the benefits of solar energy coupled with energy storage.
Sustainable Development of Silicon-Based Nanocomposite Materials for Next Generation Lithium-Ion Batteries For Electric Vehicles

Chris Yuan, Case Western Reserve University, Cleveland, Ohio, United States.

Current lithium ion batteries used on board of electric vehicles have small energy density due to the small specific capacity of electrode materials used. Silicon nanomaterials, with high specific capacity, are widely recognized as promising anode materials for next generation lithium ion batteries. However, current manufacturing processes developed for producing silicon nanomaterials for lithium ion batteries have significant sustainability issues in terms of heavy use of toxic chemicals, generation of nanoparticle emissions, and high energy consumptions. In this presentation, we will report our most recent results on sustainable development of silicon-based nanocomposite materials for next generation lithium ion batteries. Both mathematical modeling and experimental studies have been employed to study the process wastes and emissions from silicon nanomaterial fabrications. Life cycle assessment (LCA) has also been employed to evaluate the cradle-to-grave environmental impacts of two types of lithium ion batteries using silicon nanowire and silicon nanotubes, as anode in the lithium ion battery. The results could be useful for supporting sustainable development and scale-up of silicon nanomaterials for lithium ion battery applications on electric vehicles in future.

1:30 AM ES13.04.07
A Life Cycle Analysis of Flow Battery Technologies Based on Manufacturer Specifications
Haoyang He1
Shan Tian2
Brian Tarroja2
Oladele Ogunseitan3
Scott Samuelson1 and Julie M. Schoenung1
1Materials Science and Engineering, University of California, Irvine, Irvine, California, United States;
2Mechanical and Aerospace Engineering, University of California, Irvine, Irvine, California, United States;
3Population Health and Disease Prevention, University of California, Irvine, Irvine, California, United States.

The increasing recognition of environmental impacts from the production and usage of conventional energy resources demands that electric grids must achieve high renewable energy adoptions to reduce these impacts. California has established goals to meet, by the year 2050, 100% of the electric demand with carbon-free energy resources and an 80% percent decrease in economy-wide greenhouse gas (GHG) emissions compared to 1990 levels. Meeting these goals will require the deployment of energy storage systems to manage variable renewable resources such as wind and solar. Flow batteries have the advantage of scalability to high capacities, the separation of energy and power modules, long cycle life, and fast response times. While significant research has focused on improving flow battery performance and efficiency, few studies have explored their potential environmental impacts. In this study, we perform a materials life cycle analysis to evaluate the environmental impacts of three battery chemistries. The environmental impacts associated with the raw materials extraction, product manufacturing, and product assembly are evaluated and compared using SimaPro and EcoInvent, with an emphasis on global warming potential (GWP), ozone depletion potential (ODP), particulate matter (PM), acidification (AP), eutrophication (EP), abiotic resource depletion (ADP), cumulative energy demand (CED), and eutocicity (ETP). Impacts associated with the use-phase of flow batteries were evaluated through the application of the energy systems modeling tool HiGRID. The results provide insight into the effects of product design and material selection choices on the potential environmental footprint of these novel energy storage devices.

11:45 AM ES13.04.08
Assessing the Environmental Performance of Potential Solar Absorber Cu2AsS4
Joe Andl1
Nehika Mathur2
Rakesh Agrawal1
John Sutherland2
Fu Zhao3,4 and Carol A. Handwerker1,2
1Materials Engineering, Purdue University, Lafayette, Indiana, United States;
2Environmental and Ecological Engineering, Purdue University, West Lafayette, Indiana, United States;
3Chemical Engineering, Purdue University, West Lafayette, Indiana, United States;
4Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States.

Life cycle assessments (LCAs) are a standard method to perform accurate and thorough environmental assessments on a variety of products and processes. These assessments can be used to generate data about the environmental impact of a product throughout its life cycle, and can be performed to inform decisionmakers, support policy, and guide design. Ideally for product design, LCAs will be performed at every stage throughout the development process. Practically, system and informational limitations create trade-offs between design freedom and assessment reliability: the earlier an assessment is performed the less comprehensive it can be, but the later an assessment is performed the less the design can be changed. Considering this trade-off, this work outlines a life cycle assessment that has been completed on a Cu2AsS4 semiconductor that is a strong alternative solar absorber candidate—if it can be developed sustainably.

Cu2AsS4 has recently gained attention as a solar absorber material after Yu et al.1 calculated its high absorption properties and high spectroscopic-limited maximum efficiency. Density functional theory (DFT) calculations suggest this material may be tolerant to deep defects;2 and it has been experimentally determined to have an ideal direct band gap and exhibit strong photocurrent characteristics on a natural mineral sample.1 Only recently has this material been synthesized into a thin film solar cell architecture and demonstrated a non-zero photoconversion efficiency.3 In conjunction with improving its efficiency, the objective throughout development is its sustainable design, which is particularly relevant for the development of Cu2AsS4 because of the inherent risk of developing a technology that contains arsenic. Although sustainable development must consider more than only an environmental perspective, this work serves to establish the basis of the environmental implications of this potential technology. We present a cradle-to-cradle life cycle assessment of this material and compare its potential impacts to other renewable and non-renewable energy technologies. Scenario and sensitivity analyses are completed to understand the degree of impact that design parameters have on the environmental performance. This information will lead to a discussion on considerations for the sustainable design of Cu2AsS4 solar technology.


SESSION ES13.05/ES14.01: Joint Session: Sustainable Materials Development—Promoting Green Engineering and a Circular Economy
Session Chairs: Ryan Ginder and Julie Schoenung
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 121 B

1:30 PM ES13.05.01/ES14.01.01
Panel Discussion
Carol A. Handwerker1, William Olson2, Alan Rae3, Julie M. Schoenung1 and Ashley White4; 1Purdue University, West Lafayette, Indiana, United States; 2ASM International, Phoenix, Arizona, United States; 3Incubator Works, Painted Post, New York, United States; 4University of California, Irvine, Irvine, California, United States; 5Lawrence Berkeley National Laboratory, Berkeley, California, United States.

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2:30 PM BREAK

3:30 PM ES13.05.02/ES14.01.02
Validation of Ostrom Principles to Support the Circular Economy in Used Electronics
Mark Schaffer, Carol A. Handwerker and William Olson; iNEMI, Pflugerville, Texas, United States.

Metals recovery from electronic product recycling is currently focused on high-volume metals that are easily recoverable and on low-volume, high-value precious metals. Current and future electronics will increasingly contain small quantities of materials which are not currently recovered in today’s recycling infrastructure. Trends toward miniaturization, product dematerialization, and increasing materials heterogeneity create increasing challenges with respect to materials recovery, and the financial viability of electronics recycling
generally. In particular, the project examined whether conditions exist in the electronics and recycling industries to develop a voluntary, community-based solution involving adaptive governance systems to self-manage used electronics as common pool resources. This concept was inspired by the work of Dr. Eleanor Ostrom (2009 Nobel Laureate in Economics). It was concluded that the necessary conditions do exist, and that the time was right to take the next steps. Therefore, the International Electronics Manufacturing Initiative (iNEMI) undertook a collaborative project to examine the role its members could play in increasing materials recovery, while promoting sustainable electronics. The main take-home message from the project was that the situation is bad and getting worse if we consider materials recovery as the only option for end-of-use (EoU) electronics. As a result of that project, a new iNEMI project was then launched to focus on value recovery from hard disk drives (HDDs), including multiple existing and possible future dimensions of an EoU system that could improve its effectiveness, financial viability, and sustainability. The dimensions examined ranged from reuse and remanufacturing of HDDs to reuse of components, transformation of components for use in other applications, and recycling of critical materials as well as commodity materials being lost under the existing recycling paradigm. The project aims to study and implement a proof of concept of the necessary conditions and issues involved to develop a voluntary, community-based solution involving adaptive governance systems to self-manage common pool resources. Though the focus is on the reuse and recovery of spinning media (Hard Disk Drives) and rare earth magnets, the principles can be applied to any used electronic product.

It includes:
- Identifying Criteria for Enabling Reuse of used, functioning HDDs and of components from used, non-functioning HDDs
- Identifying Criteria for Enabling Reuse of HDD components in HDD applications – both direct and indirect for metal components, disks, magnets, motors, head, PWBs etc.
- Identifying Criteria for Enabling Reuse of magnets in non-HDD applications

Developing economic and logistics estimates for cases studies

Establishing necessary Design principles for the system for value recovery

Conducting a Demonstration project on HDD recovery to validate the principles identified

Benchmarking the current reuse and recovery (direct, indirect) and barriers with stakeholder input

Identifying the Leverage Points, mapping the supply chain, and identifying key gaps for developing a circular economy including each value pathway for HDDs

A Practical Means for Assessing Circular Economic Value of an ICT Product Mark Schaffer, iNEMI, Pflugerville, Texas, United States.

A review of existing recyclability and reusability metrics revealed that the industry has limited means of practically assessing circular economic value (recyclability, reusability, reparability and refurbishabilty) of an ICT product. Current mass-based metrics, in their most simplistic form, are deficient. Product designers control material and design choices which affect downstream end-of-life costs, while the market controls the materials that are recovered. Yet, no metric or guidance links these attributes together. The iNEMI Reuse and Recycling Metrics Project team has been developing a practical means for assessing the circular economic value of an Information and Communication Technology (ICT) product with the focus on incorporating score factors that assign reasonable impact value to product design features along with the ability to recover (whole products, parts) and return value (from, recycling and/or energy recovery) back to the market. Included in this scoring factor are highlighted aspects that are within the product designer’s control such as material choice and ease of liberation of components and materials and those aspects outside the product designer’s control such as the availability of recovery for reuse/recycling technologies in the markets where the product is placed. The metric assigns a reasonable impact value based on the design and a weighted recovery rate, which brings the actual results into the traditional mass-based metrics. The project is developing an assessment tool for the ability to disassemble a product for repair, reuse, parts harvest, material recovery, or energy recovery/landfill.

ICT stakeholders, including product designers, manufacturers, customers, recyclers, governmental authorities, and environmental advocates can use this means to assess the relative impact of product design choices early in the product life cycle. This will benefit both the industry and the environment to achieve sustainability. The intention for the metric is to identify gaps that prevent return to market value by highlighting the most impactful action(s) needed to close the gaps, and to inform product designers and manufacturers of the end-of-life impacts of their decisions.


The recycling of waste electrical and electronic equipment (WEEE) has been a great challenge for the recycling industry in the last decades. Predictions on the future volume of such waste shows that it will rapidly increase during the coming years (Baldev et al., 2015). Some of the waste fractions derived from WEEE are considered to be hazardous, since they contain toxic compounds restricted by the Directive of EU (2002) for Hazardous substances in WEEE. Therefore, the scientific community are focusing on finding alternative processes in order to minimise their environmental impacts and eliminate the risk of human exposure during recycling. Previous studies have investigated several processes for recycling of WEEE in terms of materials or energy. Pyrolysis is one of the alternatives which combines both energy and partially materials recovery through its production of oil and gas. Moreover, the solid residue, which contains high percentage of metals in non-oxidised form can be recovered through hydrometallurgical process.

The current study involves the decomposition of three representative WEEE fractions, collected at a recycling plant located in Sweden focusing on feedstock recycling. The experiments are performed in a thermogravimetric analyser (TGA) in order to evaluate their decomposition behaviour. Furthermore, pyrolysis experiments have been performed at different temperatures (300-700 oC) in order to correlate the pyrolysis products with the choice of temperature. Through these experiments a kinetic study has been performed aiming to design a process that can maximize the production of specific organic compounds while minimizing the evolution of brominated compounds, which are usually present in the oil (Evangolopoulos 2015).

Tests were also performed in a semi industrial continuous pilot plant designed to treat 1kg of WEEE per hour. The experiments examine the possibility of releasing less brominated compounds according to the different tested temperature conditions. Moreover, the properties of the oils obtained by the process was also investigated experimentally in order to conclude to the application of this as a new material for feedstock recycling or for energy purposes. Finally, the results shows a route that should be followed for implementing pyrolysis in order to minimize the material and energy losses in the concept of circular economy towards a more sustainable way of recycling the WEEE.

Life Cycle Assessment of Bioleaching in Rare Metals Recovery Annemarie Falké1 and Michael Höck2; 1Institute of Business Administration, esp. Resource Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany; 2Institute of Industrial Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany.

In light of growing demand and pollution versus a finite amount of resources, electronic waste recycling is a way towards material circularity. Due to the complex composition of end of life products and the physical characteristics of the materials, it becomes more difficult to recover pure metals from the waste stream. Especially rare metals, which, although abundant in the earth’s crust, only occur in low concentrations, are a sought after commodity as they are important for the economy and are found in numerous products.

The novel existent technology of using bioleaching as a hydrometallurgical process to win indium from electronic waste will be assessed exemplarily. This presentation will focus on preliminary results of batch trials in a lab scale bioreactor, whereby Indium was recovered from the electronic waste recycling process. Hereby Life Cycle Assessment is used to
4:30 PM ES13.05.06/ES14.01.06
Closing the Loop on Fiber Reinforced Composite Materials Ryan S. Ginder, 1, 2 and Soydan Ozcen; 1, 2 Mechanical, Aerospace and Biomedical Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 1 Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

In the push for a more sustainable economy, fiber reinforced polymer composites (FRPCs) have proved an important component in implementing this vision. FRPCs have improved energy efficiencies in the transportation sector through the lightweighting of vehicles, such as aircraft and cars, and have enabled alternative energy technologies such as wind. The increasing use of FRPCs, however, has led to a corresponding increase in composite waste, such as production scrap from carbon fiber composite aircraft and accumulating end of life wind turbine blades. Up until the last half decade or so, no successful techniques for recycling these materials existed resulting in near 100% of all FRPCs being destined for landfill. Recent successes repurposing waste-to-energy pyrolysis technology, already developed for the processing of feedstocks like e-waste, have resulted in accumulating end of life wind turbine blades. Recent successes repurposing waste-to-energy pyrolysis technology, already developed for the processing of feedstocks like e-waste, have resulted in accumulating end of life wind turbine blades. In these pyrolysis systems, polymer matrix materials are converted to energy while the reinforcing fiber is reclaimed for 2nd generation (and beyond) composite production.

In this talk, research efforts to extend the success of rCF to the recycling of glass fiber reinforced composites (GFRCs) will be discussed. GFRCs comprise over 90% of all FRPC production; however, they also exhibit numerous technical challenges that have limited progress in their recovery. Emphasis will be placed on addressing glass fiber embrittlement incurred during pyrolysis processing and re-engineering fiber surface chemistry for redispersion in new polymer resins. Optimized recovery and postprocessing are essential for producing recycled glass fiber (rGF) of sufficient value that can economically support a rGF industry and begin closing the loop on FRPC materials writ large. Discussion will also include details from initial pilot plant scale pyrolysis trials completed in partnership with the Institute for Advanced Composites Manufacturing Innovation (IACMI) and the American Composites Manufacturers Association (ACMA).

4:45 PM ES13.05.07/ES14.01.07
Characterisation and Determination of the Industrial Potentials of Ugwuaji Clay Deposit Nkem E. Nwankwo; Metallurgical and Materials, Nnamdi Azikiwe University, Awka, Nigeria.

A characterisation study of a virgin clay deposit has been undertaken from Ugwuaji clay deposit in Enugu South Local Government area of Enugu State. The work done consist of chemical analysis, morphology and microanalysis of sample clay with Scanning Electron Microscope equipped with energy dispersive spectrometer (EDS), the major elements are determined by X-ray Fluorescence (XRF), the relative phase quantities of wt% and phases estimated and identified with X-ray Diffraction (XRD), technique and the chemical analysis by Atomic Absorption Spectrometer (AAS) analysis. The results obtained from the investigation show that the clay sample is aluminosilicate refractory and it is within the range of foreclay (25-45% alumina). The potential utilisation of clay for firebricks production for furnace lining is in consideration. It is concluded that mineralogical composition and structure are the application determination parameters.

SYMPOSIUM ES14

Materials Circular Economy for Urban Sustainability
April 24 - April 24, 2019

Symposium Organizers
Jean-Christophe Gabriel, CEA
Sahajwalla Veena, University of New South Wales
Yan Wang, Worcester Polytechnic Institute
Qingyu Yan, Nanyang Technological University

* Invited Paper

SESSION ES14.01/ES13.05: Joint Session: Sustainable Materials Development—Promoting Green Engineering and a Circular Economy
Session Chairs: Ryan Ginder and Julie Schoenung
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1:30 PM ES14.01.01/ES13.05.01
Panel Discussion Carol A. Handwerker; 1, 2, William Olson; 1, 2, Alan Rae; 1, 2, Julie M. Schoenung; 1, 2 and Ashley White; 1, Purdue University, West Lafayette, Indiana, United States; 2 ASM International, Phoenix, Arizona, United States; 3 Incubator Works, Painted Post, New York, United States; 4 University of California, Irvine, Irvine, California, United States; 5 Lawrence Berkeley National Laboratory, Berkeley, California, United States.

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3:45 PM ES14.01.04/ES13.05.04
Life Cycle Assessment of Biodeaing in Rare Metals Recovery

Ammerlie Falke 1 and Michael Höck 2; 1 Institute for Business Administration, esp. Resource Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany; 2 Institute of Industrial Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany.

In light of growing demand and pollution versus a finite amount of resources, electronic waste recycling is a way towards material circularity. Due to the complex composition of end of life products and the physical characteristics of the materials, it becomes more difficult to recover pure metals form the waste stream. Especially rare metals, which, although abundant in the earth’s crust, only occur in low concentrations, are a sought after commodity as they are important for the economy and are found in numerous products.

New recycling technologies not only face technical difficulties but also need to overcome challenges of feasibility in both economic and environmental aspects. An assessment regarding environmental impacts and economic factors at the early development stages of such technologies is necessary to ensure a successful establishment. Bioleaching has been specifically applied in copper recovery since the 16th century and is now also used to win metals such as zinc, gold or cobalt. Using this hydrometallurgical approach for the recovery of by-metals such as sodium in an innovative approach in the first development stages. Indium-rich material such as electronic waste is leached in a bioreactor as opposed to the environmentally risky heap leaching. The beneficiation process of indium from electronic waste can be classified into four steps. In a first step, the material is crushed and comminuted. The fines are then fed into a bioreactor, where biodeaing takes places in multiple stages. The third and fourth steps are the solvent extraction and subsequent recovery of the target metal from the solution. In a combined process, indium rich tailings and primary ores could also be added in the reactor to ensure a stable input and independence of the amount of end-of-life products.

A review of existing recyclability and reusability metrics revealed that the industry has limited means of practically assessing circular economic value (recyclability, reusability, reparability and refurbish-ability) of an ICT product. Current mass-based metrics, in their most simplistic form, are deficient. Product designers control material and design choices which affect downstream end-of-life costs, while the market controls the materials that are recovered. Yet, no metric or guidance links these attributes together. The iNEMI Reuse and Recycling Metrics Project team has been developing a practical means for assessing the circular economic value of an Information and Communication Technology (ICT) product with the focus on incorporating score factors that assign reasonable impact value to product design features along with the ability to recover (whole products, parts) and return value (from reuse, recycling and/or energy recovery) back to the market. Included in this scoring factor are highlighted aspects that are within the product designer’s control such as material choice and ease of liberation of components and materials and those aspects outside the product designer’s control such as the availability of recovery for reuse/recycling technologies in the markets where the product is placed. The metric assigns a reasonable impact value based on the design and a weighted recovery rate, which brings the actual results into the traditional mass-based metrics. The project is developing an assessment tool for the ability to disassemble a product for repair and recovery of whole product, components and parts.

The resulting system assesses the environmental feasibility and physical practicality to separate and liberate the parts, components and materials from ICT type products when whole product reuse is not possible. The assessment is divided into three tiers; material choice, ease of liberation and the downstream recycling technology. Regional factors have also been researched and incorporated in the assessment criteria. Additionally, the team reviewed the hierarchy of recovery, which impacts the ease of returning value to the market: repair and reuse, parts harvesting, material recovery, or energy recovery/landfill.

ICT stakeholders, including product designers, manufacturers, customers, recyclers, governmental authorities, and environmental advocates can use this means to assess the relative impact of product design choices early in the product life cycle. This will benefit both the industry and the environment to achieve sustainability. The intention for the metric is to identify gaps that prevent return to market value by highlighting the most impactful action(s) needed to close the gaps, and to inform product designers and manufacturers of the end-of-life impacts of their decisions.

4:00 PM ES14.01.04/ES13.05.04
Pyrolysis and Detoxification of Waste Electrical and Electronic Equipment (WEEE) for Feedstock Recycling

The recycling of waste electrical and electronic equipment (WEEE) has been a great challenge for the recycling industry in the last decades. Predictions on the future volume of such waste shows that it will rapidly increase during the coming years (Baldé et al., 2015). Some of the waste fractions derived from WEEE are considered to be hazardous, since they contain toxic compounds restricted by the Directive of EU (2002) for Hazardous substances in WEEE. Therefore, the scientific community are focusing on finding alternative processes in order to minimise their environmental impacts and eliminate the risk of human exposure during recycling. Previous studies have investigated several processes for recycling of WEEE in terms of materials or energy. Pyrolysis is one of the alternatives which combines both energy and partially materials recovery through its production of oil and gas. Moreover, the solid residue, which contains high percentage of metals in non-oxidised form can be recovered through hydrometallurgical process.

The current study investigates the decomposition of three representative WEEE fractions, collected at a recycling plant located in Sweden focusing on feedstock recycling. The experiments are performed in a thermogravimetric analyser (TGA) in order to evaluate their decomposition behaviour. Furthermore, pyrolysis experiments have been performed at different temperatures (300-700 °C) in order to correlate the pyrolysis products with the choice of temperature. Through these experiments a kinetic study has been performed aiming to design a process that can maximize the production of specific organic compounds while minimizing the evolution of brominated compounds, which are usually present in the oil (Evangelopoulos 2015).

Tests were also performed in a semi industrial continuous pilot plant designed to treat 1kg of WEEE per hour. The experiments examine the possibility of releasing less brominated compounds according to the different tested temperature conditions. Moreover, the properties of the oils obtained by the process was also investigated experimentally in order to correlate the pyrolysis products with the choice of temperature. Through these experiments a kinetic study has been performed in order to minimize the material and energy losses in the concept of circular economy towards a more sustainable way of recycling the WEEE.

4:15 PM ES14.01.05/ES13.05.05
Life Cycle Assessment of Biodealing in Rare Metals Recovery

Ammerlie Falke 1 and Michael Höck 2; 1 Institute for Business Administration, esp. Resource Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany; 2 Institute of Industrial Management, Technische Universität Bergakademie Freiberg, Freiberg, Germany.

In light of growing demand and pollution versus a finite amount of resources, electronic waste recycling is a way towards material circularity. Due to the complex composition of end of life products and the physical characteristics of the materials, it becomes more difficult to recover pure metals form the waste stream. Especially rare metals, which, although abundant in the earth’s crust, only occur in low concentrations, are a sought after commodity as they are important for the economy and are found in numerous products.

New recycling technologies not only face technical difficulties but also need to overcome challenges of feasibility in both economic and environmental aspects. An assessment regarding environmental impacts and economic factors at the early development stages of such technologies is necessary to ensure a successful establishment. Bioleaching has been specifically applied in copper recovery since the 16th century and is now also used to win metals such as zinc, gold or cobalt. Using this hydrometallurgical approach for the recovery of by-metals such as sodium in an innovative approach in the first development stages. Indium-rich material such as electronic waste is leached in a bioreactor as opposed to the environmentally risky heap leaching. The beneficiation process of indium from electronic waste can be classified into four steps. In a first step, the material is crushed and comminuted. The fines are then fed into a bioreactor, where biodeaing takes places in multiple stages. The third and fourth steps are the solvent extraction and subsequent recovery of the target metal from the solution. In a combined process, indium rich tailings and primary ores could also be added in the reactor to ensure a stable input and independence of the amount of end-of-life products.

A new existing technology of using biodeaing as a hydrometallurgical process to win indium from electronic waste will be assessed exemplarily. This presentation will focus on preliminary results of batch trials in a lab scale bioreactor, whereby Indium was recovered from the electronic waste recycling process. Hereby Life Cycle Assessment is used to determine the ecological factors. Further, the environmental risks connected to this technology are summarized and put into perspective. LCA offers a standardized opportunity to determine the environmental impacts over the life cycle of a given product but can be applied to processes. The data is used to establish the feasibility of this recycling technology including both economic and ecologic parameters.
characteristic study of a virgin clay deposit has been undertaken from Uguwuji clay deposit in Enugu South Local Government area of Enugu State. The work done consists of chemical analysis, morphology and microanalysis of sample clay with Scanning Electron Microscopy equipped with energy dispersive spectrometer (EDS), the major elements are determined by X-ray Fluorescence (XRF), the relative phase quantities of wt% and phases estimated and identified with X-ray Diffraction (XRD), technique and the chemical analysis by Atomic Absorption Spectrometer (AAS) analysis. The results obtained from the investigation show that the clay sample is aluminosilicate refractory and it is within the range of foreclay (25-45% alumina). The potential utilisation of clay for firebreaks production for furnace lining is in consideration. It is concluded that mineralogical composition and structure are the application determination parameters.

SYMPOSIUM ES15

Fundamental Understanding of the Multifaceted Optoelectronic Properties of Halide Perovskites

April 23 - April 26, 2019

Symposium Organizers
Pablo Boa, University of Valencia
Yabing Qi, Okinawa Institute of Science and Technology
Tze Chien Sum, Nanyang Technological University
Carolin Sutter-Fella, Lawrence Berkeley National Laboratory

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* Invited Paper

SESSION ES15.01/ES16.03/ES17.03: Joint Session: Halide Perovskites—Celebrating the 10th Anniversary of Perovskite Solar Cell Invention (JACS, 2009, 131, 6050)
Session Chairs: Tze Chien Sum and Yuanyuan Zhou
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 125 AB

10:30 AM *ES15.01.01/ES16.01.01/ES17.03.01
Present Status and Next Important Challenge of Perovskite Photovoltaics Towards Industrialization Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Power conversion efficiency (PCE) of lead halide perovskite solar cell (over 23%) has surpassed those of CIGS and CdTe, approaching the top value of crystalline Si cell. Our group has been able to achieve PCE over 21% by low cost ambient fabrication. However, high PCE of single-cell enabled by lead halide-based perovskite absorbers are now being saturated, taking the Shockley Queisser (SQ) limit of open-circuit voltage \( V_{OC} \) (ca.1.32V) into account. Tandem cell making, which can further increases PCE up to 28% or more, leads to higher material and process cost and will raise a question if performance/cost ratio can be accepted in industry. Therefore, a smart way is to create a single cell which has high PCE comparable with that of GaAs (>28%) by reducing bandgap energy to <1.4 eV without accompanied of increase in \( V_{OC} \) loss. This possibility will be in a family of metal halide perovskite out of those depending on use of lead. In addition to such efficiency issue, high performance of organo lead halide materials is not compatible with robust high stability required for practical use. Ensuring the intrinsic thermal stability (desirably >200°C) of the perovskites is a key issue before industrialization. In addition, toxicity of lead-based perovskites are going to become the most formidable challenges for real use (commercialization), in particular, for applications to IoT society, which is one of the most promising field of perovskite photovoltaic device in terms of high voltage output even under weak illumination. These thoughts urge us to concentrate our next research of perovskite photovoltaics (PV) more on development of non-lead high efficiency absorbers. Sn perovskite is still a strong candidate because Sn(II) has been found to be stabilized against ambient air by metal doping method (such as Ge). Regarding Bi-based perovskites, we found AgBiI_3 as a promising all-inorganic absorber having high thermal and moisture stability. Stability also highly depends on the property of charge transport materials (CTMs), especially, the kind of hole transporter. Spiro-OMeTAD does not work at high temperature while P3HT, for example, is thermally stable. In our collaboration with JAXA, P3HT-based perovskite devices showed robust stability by exposure to high (100°C) and low (-80°C) temperatures and also to high energy particle radiations (Science, 2018, 2, 148). Selection of CTMs is another important key in combination with non-lead perovskite materials. In conclusion, next direction of perovskite PV should be to enhance PV performance of non-lead all-inorganic semiconductor materials by extended compositional engineering, in parallel with developing thermally stable CTMs. Our on-going studies on non-lead perovskite materials in our group will be introduced in the talk.

11:00 AM *ES15.01.02/ES16.01.02/ES17.03.02
Issues and Solutions in Perovskite Solar Cells Nam-Gyu Park; Sungkyunkwan University, Suwon, Korea (the Republic of).

Since the first report on the high efficiency, stable solid-state perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 23.3% in 2018. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches already over 10,000 as of October 2018, which is indicative of a paradigm shift in photovoltaics. Although small area cell exhibited superb efficiency surpassing the performance of thin film technologies, scale-up technology is required toward commercialization. In addition, further higher efficiency toward Shockley–Queisser limit is required in is parallel. In this talk, Large-area coating technology is introduced using perovskite cluster embedded coating solution,
followed by brief introduction on history of perovskite solar cell. Bi-facial stamping method was developed for not only scale-up technique but also interface modification and low-temperature phase stabilization. For higher efficiency, managing recombination is critical. Methodology reducing recombination is developed via interface and bulk engineering. Current-voltage hysteresis is also discussed because hysteresis is related to the stability of perovskite solar cell. Ion migration is now visualized and confirmed to correlate with hysteresis.

11:30 AM ES15.01.03/ES16.01.03/ES17.03.03
Hybrid Halide Perovskite Semiconductors—An Historical Perspective
David B. Mitzi; Duke University, Durham, North Carolina, United States.

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable band gaps and relatively benign defects and grain boundaries for systems based on Group 14 metals (e.g., Ge, Sn and Pb) [2]. Indeed, these materials have enabled unprecedented rapid improvement in perovskite photovoltaic performance to levels above 20% power conversion efficiency and with open circuit voltages above 1 V for a single junction photovoltaic (PV) device [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility [4,5], semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.


SESSION ES15.02: Perovskite Composition and Defects Engineering I
Session Chairs: Jacques-E. Moser and Tom Savenije
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 130

1:30 PM ES15.02.01
Towards Highly Emissive Halide Perovskites for Optoelectronic Applications
Samuel D. Stranks; Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Metal halide perovskites are exciting materials for a range of optoelectronic devices. One of their most tantalizing features is the potential for tunable emission with high luminance yields. Such properties are promising for reaching the radiative efficiency limits in single and multi-junction solar cells as well as color-tunable light-emitting diodes. However, there are a number of challenges in attaining high luminance yields and color stability across a range of bandgaps.

Here, I will present a select portion of our ongoing work to understand the origin of non-radiative losses in a range of halide perovskite films, crystals and device systems, and how we can use this information to push materials and devices towards their efficiency limits. We use a selection of nano- and micro-scale imaging techniques including photoluminescence, photo-emission and nano-X-Ray-Diffraction microscopy to visualise the impact of defects and strain on local charge carrier recombination. We also employ passivation techniques designed to remove these spatially heterogeneous losses, which we demonstrate on small and large bandgap bulk 3D perovskites and 2D confined perovskite nano-platelets. Finally, we show that these approaches ultimately lead to improved solar cell and LED performance and bandgap stability.

2:00 PM ES15.02.02
Atomic Scale Analysis of Perovskite CH₃NH₂PbI₃ Ultra-Thin Films by Scanning Tunneling Microscopy
Afshan Jamshaid, Robin Ohmann, Jeremy Hieulle, Collin Stecker, Luís K. Ono and Yabing Qi; Okinawa Institute of Sciences & Technology, Tancha, Japan.

In recent years, the organic-inorganic hybrid perovskite has gained an increasing research interest in academia for applications in thin film solar cells, due to rapidly increased efficiency (from 3.8 to 23.3% within a decade) [1], high absorption coefficient [2], low-cost fabrication process, and material availability [3]. Among the hybrid perovskites, MAPbI₃ (CH₃NH₂PbI₃) based solar cells have shown high power conversion efficiencies but with several obstacles such as thermal instability, hysteresis loss at room temperature. Therefore, the commercialization of these solar cells is still a challenge. Understanding and resolving these issues necessitate the investigation of the sample at the atomic scale to determine the underlying fundamental processes.

Here, we present the growth and experimental characterization of thin MAPbI₃ films on Au (111) under ultra-high vacuum conditions (UHV=1x10⁻¹⁰ Torr). The thin films were prepared by vacuum evaporation of the precursor molecules MAI and PbI₃ with a thickness of a few monolayers (approx. 4 nm). We characterize the sample with scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS), obtaining information about the atomic structure, and chemical composition. For the electronic properties analysis, we used ultraviolet photoemission spectroscopy (UPS), and inverse photoemission spectroscopy (IPES). Our study will provide the basis for further understanding ion incorporation and stability at the atomic scale.

Reference

2:15 PM ES15.02.03
Concentration and Precursor Delivery Effects on Hybrid Perovskites Deposited by Resonant Infrared Matrix-Assisted Pulsed Laser Evaporation
Enrique T. Barraza1, Niura Wright1, Maria Folgueras1, Ankst Rastogi2, Ruipeng Li1, Masafumi Fukuda2 and Adrienne Stiff-Roberts1,2, 'Electrical & Computer Engineering, Duke University, Durham, North Carolina, United States; 'National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States; 'University Program in Materials Science & Engineering, Duke University, Durham, North Carolina, United States.

Hybrid organic-inorganic perovskites possess a diverse set of properties that make them excellent materials for a variety of applications. New perovskite compounds with complex structures and novel properties promise to further expand the applicability of this class of materials, but may require new processing approaches to be synthesized. Issues of solubility and degradation in the synthesis of complex perovskites can be addressed via resonant infrared matrix-assisted pulsed laser evaporation (RIR-MAPLE). RIR-MAPLE is a physical vapor deposition technique that has been shown to deposit perovskite materials in a manner that preserves the integrity of the perovskite components and maintains the composition of the target source. [1, 2] Because RIR-MAPLE uses lower concentration solutions to form frozen targets (compared to conventional approaches) and has different deposition schemes available to deliver precursors to the substrate, [3] it is uniquely positioned to act as a framework for studying complex perovskites with limited solubility.

Using CH₃NH₂PbI₃ (methylammonium lead triiodide, or MAPbI₃) as an initial model system, the effects of RIR-MAPLE solution concentration and deposition scheme were studied. Because MAPbI₃ can easily be spin-cast and its properties have been widely studied, it acted as a reference to compare any effects of RIR-MAPLE deposition on material properties.

Baseline (21.7 mM) concentrations of CH₃NH₃I (methylammonium iodide, or MAI) and PbI₂ were increased by a factor of 1.5 times to yield solutions that had high inorganic,
high organic, and high overall component concentrations. Reference spin-casting solutions were created by using 1.4 and 1.6 M concentrations of MAI and PbI₂ to create the same relative non-stoichiometric conditions as in the RIR-MAPLE solutions. Also, a small amount (~20 µL) of monooethylene glycol (MEG) was added to additional spin-cast solutions to observe possible effects on material properties because this chemical serves as a co-matrix to resonantly absorb laser energy during RIR-MAPLE deposition.

RIR-MAPLE deposition schemes based upon multiple source solutions within a partitioned target cup were adapted for MAPbI₂ to drastically alter how perovskite precursors are delivered to the chosen substrate. Substrate temperatures were controlled across all deposition schemes to observe any effects on how precursors react in these schemes.

The crystallographic properties of all films were studied using X-ray diffraction (XRD) and synchrotron grazing-incidence wide-angle X-ray scattering (GIWAXS). Film morphology was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optoelectronic properties of the films were determined by photoluminescence and UV-Visible absorbance spectrosopies.

This work is important to establish fundamental growth mechanisms of perovskite thin films deposited by RIR-MAPLE and expands upon previous foundational studies. By demonstrating versatility in solution compositions and deposition schemes, RIR-MAPLE is positioned favorably to address the requirements to synthesize complex perovskite materials systems.

This research used beamline 11-BM of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704.

We gratefully acknowledge support from the Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE) an Energy Frontier Research Center funded by the Office of Basic Energy Sciences, Office of Science within the US Department of Energy.

References:

2:30 PM ES15.02.04 Unraveling the Impact of Halide Mixture on Charge Carrier Mobility via Scanning Tunneling Microscopy and Photoluminescence Electronic Spectroscopy: Jeremy G. Hsieh¹, Xiaoming Wang², Collin Stecker³, Dae-Yong Son¹, Longbin Qiu¹, Robin Ohmann¹, Luis K. Ono¹, Aitor Mugaza³, Yafiu Yan³ and Yabing Qi²; Okinawa Institute of Science and Technology Graduate University (OIST), Onna, Japan; ³Department of Physics and Astronomy and Wright Center for Photovoltaics Innovation and Commercialization, The University of Toledo, Toledo, Ohio, United States; ¹Catalan Institute of Nanoscience and Nanotechnology (ICN2), Consejo Superior de Investigaciones Científicas (CSIC) and The Barcelona Institute of Science and Technology, Barcelona, Spain; ²ICREA-Institució Catalana de Recerca i Estudis Avançats, Barcelona, Spain.

Organic-inorganic perovskite solar cells are currently under the spotlight. Despite numerous advantages, their poor stability hinders commercialization of perovskite-based devices. To increase perovskite stability various strategies have been envisaged [1]. Mixing different halides (I, Br, CI) has been shown both experimentally and theoretically to have a strong impact on the device performance and stability [2-5]. However, the stabilizing effect of the halides critically depends on their distribution in the mixed compound, a topic that is currently under intense debate [6-8]. A fundamental understanding remains largely elusive regarding the correlation between the structure of the mixed-perovskites and their electronic properties at the atomic level.

In this work, combining scanning tunneling microscopy (STM), density functional theory (DFT) and UV/X-ray photoelectron spectroscopy (UPS/XPS), we reveal the exact location of I and Cl anions in the mixed CH₃NH₃PbBr₂I and CH₃NH₃PbBr₂Cl perovskite lattices. Additionally, we demonstrate the impact of halide-incorporation on the material electronic properties and stability. Furthermore, we determine the ideal Cl-incorporation ratio for stability increase without detrimental bandgap modification. The increased material stability induced by chlorine incorporation is verified by performing photoluminescence spectroscopy on a device architecture. Our findings provide an important direction for the fabrication of stable perovskite devices.

References:

2:45 PM ES15.02.05 Role of Different Cations (MA⁺, FA⁻ and Cs⁺ and Rb⁺) on Charge Carrier Recombination in Perovskite Solar Cells Ankur Solanki, Swee Sien Lim and Tze Chien Sum; Nanyang Technological University Singapore, Jurong West, Singapore.

Incorporation of inorganic cations has been recently demonstrated a technique to enhance the efficiency and lifetime in perovskite solar cells. However, the understanding and correlation of ultrafast photophysics in relation to opto-electrical properties to the device performance are still lacking. Here, we systematically analysis the role of inorganic cations on the photophysics using photoluminescence techniques and correlate with photovoltaic properties. The lack of the integration of Rb⁺ with organic cations MAFA (MA, methylammonium, and FA, formamidinium,) leads to higher defect density and trap-assisted monomolecular recombination in thin films. While, the incorporation of Cs⁺ increases the perovskite grain size and shows longer charge carrier lifetime by mitigating the defects to enhance the power conversion efficiency (PCE); indicating the better incorporation of Cs⁺ to MAFA. While the concomitant presence of Rb⁺ with Cs⁺, delay the non-radiative losses by suppressing the defect density significantly in quaternary-cation based photovoltaic system (RbCsMAFA) compared to double-cation MAFA system. Lower defects density and a more balanced charge carrier diffusion length results the PCEs over 19% in quaternary-cation-perovskites though photoluminescence quantum yield (PLQY) is comparable. While the concomitant incorporation of Rb⁺+Cs⁺ is the key to suppress the defects and charge carrier recombination for efficient photovoltaics, solitary integration of Rb⁺ with MAFA is still a challenge.

3:00 PM BREAK

SESSION ES15.03: Carrier Dynamics—Carrier Recombination and Hot Carriers I
Session Chairs: Libai Huang and Koichi Yamashita
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 130

3:30 PM ES15.03.01 How Charge Carrier Dynamics are Affected by Light Soaking and Additives in (Mixed) Metal Halide Perovskites Dengyang Guo¹, Eline Hutter¹, Zahra Andaji Garmaroudi², Mojtaba Abdi-Jalebi², Samuel Stranks² and Tom Savchenko¹; ¹Delft University of Technology, Delft, Netherlands; ²University of Cambridge, Cavendish Laboratory, Cambridge, United Kingdom.
Due to their unique opto-electronic properties, metal halide perovskites are of great interest as solar energy material. At present, non-radiative losses prevent solar cell efficiencies to reach their theoretical maximum. In this work we suppressed the non-radiative decay in methylammonium lead iodide (MAPbI₃) layers by exposing them to a light soaking treatment under ambient conditions. First of all, this treatment leads to an increase of the PL quantum efficiency from < 1% to 50%. Additionally, photo-induced time-resolved microwave conductivity (TRMC) data demonstrate that while the mobility and the trap density remain constant, the light soaking treatment reduces the non-radiative band-to-band recombination between electrons and holes. We attribute the enhancement in effective carrier lifetimes to an increased fraction of radiative recombination, leading to enhanced light soaking studies were extended to mixed cation, mixed halide perovskites, (FAₓNaᵧMAₓ(1−ξ)CsₓSnₓ)₂Pb₃I₁₀Brₓ (ξ ≤ 0.2) which are known to undergo phase separation under continuous illumination. For x < 0.5 we find that on light soaking in a nitrogen environment, the charge carrier lifetime increases, while for x > 0.5 the lifetime shortens. By analysing the TRMC traces, we propose that for x < 0.5 light soaking leads to a reduction of charge trapping in shallow states. Next, we investigate how additives such as K⁺, Cs⁺ and Rb⁺ affect the mobility and decay kinetics of photo-induced excess carriers in metal halide perovskites. The above results help to provide a framework for which cation and halide composition the best performance and stability can be expected.


4:00 PM ES15.03.02

Grain Resolved Charge Carrier Kinetics in Chalcogenide and Perovskite Materials—A Pump-Probe Microscopy and Spectroscopy Study Elham Chadiari1, Donghyeop Shin2, Ashkan Shafiee1, Qoewe Han1, Warren Warren1 and David B. Mitzi1; 1Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States; 2Chemistry, Duke University, Durham, North Carolina, United States; 3Wake Forest Institute for Regenerative Medicine, Wake Forest School of Medicine, Winston-Salem, North Carolina, United States.

We integrate the state-of-the-art pump-probe microscope and broadband diffuse reflectance spectroscopy techniques for photophysical analysis of charge carriers in photovoltaic materials including recently introduced Cu₂BaSnS₄₋ₓSeₓ (CBTSSe) chalcogenides 1–2 and MAPb₁₋ₓCsₓI₃ perovskites. Pump-probe microscopic imaging 3 enables to localize the photoexcitation patterns and early charge carrier kinetics within the grains of only a few hundreds of nanometers and localize the kinetics of photogenerated carriers in each grain. Based on broadband diffuse reflectance transient absorption spectroscopy 4 the fingerprints of photocarrier absorption, GSB bleaching and electronic states in the vis-near IR region are investigated.

For MAPb₁₋ₓCsₓI₃ perovskite samples, we identify the formation and relaxation of excited state absorption signal (charge carrier’s absorption) within film grains by performing pump-probe microscopic imaging with pump and probe pulses at 720 nm and 817 nm respectively. The time-resolved pump-probe images show a homogeneous pattern across the majority of grains while some heterogeneity is observed across different grains. We further discuss the influence of morphological parameters such as grain size and extra additives such as PbI₂ on the excited state pattern and the ultrafast kinetics of photocarriers within grains of MAPb₁₋ₓCsₓI₃ perovskites. The ultrafast kinetics of the photogenerated carriers in both pristine state and sample with additional PbI₂ is similar, while free carrier relaxation increases for larger grains.

CBTSSe is a recently introduced alternative to Cu(In,Ga)(S,Se)₂ which are known to undergo phase separation under continuous illumination. For x < 0.5 we find that on light soaking in a nitrogen environment, the charge carrier lifetime increases, while for x > 0.5 the lifetime shortens. By analysing the TRMC traces, we propose that for x < 0.5 light soaking leads to a reduction of charge trapping in shallow states. Next, we investigate how additives such as K⁺, Cs⁺ and Rb⁺ affect the mobility and decay kinetics of photo-induced excess carriers in metal halide perovskites. The above results help to provide a framework for which cation and halide composition the best performance and stability can be expected.

We will put our results in the broader perspective of other HaP physico-chemical properties and performances of HaP-based device characteristics.

References

SESSION ES15.04: Carrier Dynamics—Carrier Recombination and Hot Carriers II
Session Chairs: David Ginger and Samuel Stranks
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 130

8:00 AM *ES15.04.01
Charge Transfer Exciton Dynamics in Mixed-Composition Perovskites and 2D-3D Layered Materials
Jacques-E. Moser; EPFL, Lausanne, Switzerland.

The constituents of hybrid organic-inorganic lead halide perovskite materials have significantly evolved since the first photovoltaic devices made out of the standard methylammonium lead triiodide (MAPI, CH$_3$NH$_3$PbI$_3$) to the latest developments relying on mixed cations, mixed anions perovskite systems and arrangements of 2D-3D layers. Indeed, it appears that mixed-composition perovskites and complex structures including a low-dimensional perovskite layer on top of a bulk three-dimensional perovskite film can perform significantly better than standard systems, via both a better short-circuit current, and a larger open-circuit voltage. These parameters, commonly used to assess the performances of photovoltaic devices, directly relate to more fundamental properties of the material: the bandgap of the absorber, determined by its electronic structure, and the ratio between radiative and non-radiative charge carrier recombination quantum yields, which depends on more complex dynamical phenomena and scattering processes. Here, we use a combination of ultrafast spectroscopic techniques to scrutinize the carrier dynamics in mixed-cations, mixed-halide lead perovskite thin films. Our results evidence the formation of charge transfer excitons (CTE) at the boundaries of domains of various halide compositions. A global analysis of photoinduced transient Stark signals shows that CTE evolve gradually from Br-rich to I-rich domains over tens to hundreds of picoseconds. Rather than constituting recombination centers, boundaries between domains of various halide compositions appear then to favor charge carrier separation by driving photogenerated holes along channels of decreasing bromide content. The ultrafast dynamics of photoinduced Stark signals observed in transient absorption spectra of 2D-3D layered perovskites prepared by use of various long-chain organic cations allowed to evidence charge transfer between domains of different dimensionality taking place in competition with energy transfer. These findings show that vectorial charge separation takes place at the interface, which is at the origin of the improved efficiency of solar cells based on structured materials embodying the low dimensional layer, when compared to pristine 3D perovskite.

8:30 AM *ES15.04.02
Long-Range Hot Carrier Transport in Hybrid Perovskites Visualized by Ultrafast Microscopy
Libai Huang; Department of Chemistry, Purdue University, West Lafayette, Indiana, United States.

The Shockley-Queisser limit for solar cell efficiency of ~33% can be overcome if hot carriers can be harvested before they thermalize. Recently, carrier cooling time up to 100 picoseconds was observed in hybrid organic-inorganic lead halide perovskites, but it is unclear whether these long-lived hot carriers can migrate long distance for efficient collection. We report direct visualization of hot carrier migration in CH$_3$NH$_3$PbI$_3$ thin films by ultrafast transient absorption microscopy, demonstrating three distinct transport regimes. Quasi-ballistic transport was observed to correlate with excess kinetic energy; resulting in up to 230 nanometers transport distance in 300 fs that could overcome grain boundaries. Instead, we observe a non-ballistic transport regime in which energetic hot carriers diffuse over tens of picoseconds and ~600 nanometers before reaching the diffusive transport limit. These new insights would allow the development of extremely thin absorber and concentrator-based solar cells, when compared to pristine 3D perovskite.

9:00 AM ES15.04.03
Utilizing Hot Carriers in Perovskite Nanocrystals for New-Generation Light Harvesting Technologies
Mingjie Li and Tze Chien Sum; School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Thermodynamic calculations revealed that single junction solar cell conversion efficiencies can exceed the Shockley-Queisser limits and reach around 66% under 1-sun illumination if the excess energy of hot photogenerated carriers is utilized before they cool down to the lattice temperature (i.e., hot-carrier solar cells). Organic–inorganic lead halide perovskite semiconductors have recently emerged as the leading contender in low-cost high-performance solar cells. The key for the realization of hot-carrier (HC) solar cell include the slow hot-carrier cooling and effective extraction of hot-carrier energies which requires fast hot-carrier injection into charge collection layer before hot-carrier cooling down to the lattice temperature. Another related approach to leverage slow HC cooling for efficient energy extraction of HCs is multiple exciton generation (MEG). MEG or carrier multiplication (CM) is a process that generates more than one electron-hole pair from the absorption of one high-energy photon (with at least twice the bandgap energy, Eg), which can boost the photovoltaic efficiencies to ~44%. Perovskite NCs with their novel slow hot-carrier cooling are therefore also highly promising candidates for MEG. In this talk, firstly we will present our recent observations that the weakly quantum confined MAPbI$_3$ nanocrystals have up to ~2 orders slower hot-carrier cooling times and around 4 times larger hot-carrier temperatures than their bulk-film counterpart. This is attributed to their intrinsic phonon bottleneck and Auger-heating effects at low and high carrier densities, respectively. Importantly, we demonstrate efficient room temperature hot-electrons extraction (up to about 83%) by an energy-selective electron acceptor layer within ~1 ps from surface-treated perovskite nanocrystal very thin films (~30 nm). These new insights would allow the development of extremely thin absorber and concentrator-type hot-carrier perovskite solar cells. In the second part, we will show our most recent works on the efficient MEG (up to ~75% in slope efficiency) with low MEG thresholds (down to ~2.25Eg) in intermediate-confined colloidal FAPbI$_3$ NCs. Efficient MEG occurs via inverse Auger process within 90 fs, afforded by the slow cooling of energetic hot carriers. These insights may lead to the realization of next generation of solar cells and efficient optoelectronic devices.

References:

SESSION ES15.05: First Principles and Computational Screening I
Session Chairs: David Ginger and Samuel Stranks
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 130

9:15 AM *ES15.05.01
Physical Properties of 2D and 3D Hybrid Perovskites—Recent Results
Jacqui Ewen; INSA Rennes, Rennes, France.

Solution-processed organometallic perovskite based solar cells have emerged as a promising thin-film photovoltaic technology. The presentation will review recent optical spectroscopy and diffraction results on monocrystals of halide perovskites, colloidal nanocrystals or thin-films. 2D multilayered phases, composed of perovskites multilayers

9:45 AM ES15.05.02 The Electronic Origin of the Thermal and Phase Instability of Metal Halide Perovskites from First Principle Tao Shu Xia; Applied Physics, Center for Computational Energy Research, Eindhoven, Netherlands.

In just a few years, perovskites solar cells (PSCs) have emerged as one of the most promising solar cell technologies. So far, the PCEs of PSCs above 22% have been reported, which is rivaling values achievable with crystalline silicon solar cells. In spite of the fast growth in the photovoltaic industry, PSCs are severely limited in their large scale applications due to instability issues. These include intrinsic instabilities of the metal halide perovskites, environmental instabilities, and device operation related instability.

In this work, we discuss the intrinsic instability of the metal halide perovskite studied by combining chemical bonding analysis of DFT electronic structure calculations and experimental degradation study using Ultraviolet–visible spectroscopy. A comprehensive set of chemical bonding analysis of DFT calculations are done for AMX$_3$ (where A=Cs, MA, FA, M=PB, Sn, X=I, Br, Cl) perovskites. Bond order, net charge, steric repulsion, and Crystal Orbital Hamilton Population (COHP) analysis reveal the relation of covalent, ionic, and metallic interactions, as well as bonding/antibonding characters with their stability, respectively. As a part of this work, Ultraviolet–visible spectroscopy of AMX$_3$ perovskites film degradation during incremental heating were carried out to probe their thermal stability. A systematic comparison of the theoretical analysis and experimental data points to the most important factors responsible for the trends in the thermal stability of AMX$_3$ perovskites.

Interestingly, this sets of chemical bonding analysis also shows promise in explaining the structural instability of metal halide perovskites, i.e. transition of black phase (3D structure) to yellow phase (2D structure). The results provide important insights in strategies for stabilizing metal halide perovskites by tuning their composition.

10:00 AM BREAK

10:30 AM ES15.05.03 Point Defect Engineering in Lead-Based Mixed Halide Hybrid Perovskites via First Principles Computations Arum Kumar Mannodi Kanakkithodi; Ji-Sang Park2; Duyen H. Cao3; Nari Jeon1; Alex B. Martinson1 and Maria K. Chan1; 1Materials Science Division, Argonne National Laboratory, Argonne, Illinois, United States; 2Department of Materials, Imperial College London, London, United Kingdom; 3Center for Nanoscale Science, Argonne National Laboratory, Argonne, Illinois, United States.

An issue of critical importance in lead-based halide perovskites, much sought-after class of semiconductors in photovoltaics (PV) research, is defects; “deep” defect levels can prove catastrophic to PV performance by causing non-radiative charge carrier combination[1], whereas impurity induced energy levels in the band gap could lead to increased absorption of sub-gap photons which can enhance efficiencies[2]. While experimental detection of defects is non-trivial and identification of the origin of defect states is usually impossible, density functional theory (DFT) calculations have been widely applied to accurately predict defect formation energies and transition levels[3]. In this work, we use DFT to study various intrinsic and extrinsic point defects in mixed bromide/chloride (MAPbBr$_3$Cl) and iodide/bromide (MAPbI$_3$Br$_y$) perovskites (MA = methylammonium) with varying compositions (y = 0, 0.75, 1.5, 2.25, 3). We observe that in MAPbI$_3$, MAPbBr$_3$ and all I-Br alloyed perovskites, vacancy defects are the dominant intrinsic defects and create shallow transition levels (i.e., energy levels close to the valence or conduction band edges), while higher energy defects create deeper levels; this is in good agreement with the computational literature[4]. The equilibrium Fermi level changes from inside the valence band (very p-type conductivity) to mid-gap (intrinsic conductivity) on going from I-Br-rich to Pb-rich chemical potential conditions. In MAPbBr$_3$Cl perovskites, it is seen that vacancy defects are again the lowest energy defects and the equilibrium Fermi level follows the same trend as in MAPbBr$_3$, but halogen vacancies (V$_{ib}$ and V$_{cl}$) create deeper levels in the band gap the higher the value of y, indicating that in mixed Br/Cl or pure Cl perovskites, there is a danger of non-radiative recombination of carriers owing to deep defect levels. In order to study the influence of extrinsic point defects on the optoelectronic properties as determined by dominant intrinsic defects, we further performed high-throughput density functional theory computations to study all elements from periods II to VI of the periodic table as substituents at the Pb-site in MAPbBr$_3$, MAPbBr$_3$Cl$_y$ and MAPbCl$_3$. Our results revealed that several transition metals like Sc, Y, Zr, Nb and Hf create lower energy substitutional defects than the dominant intrinsic defects in the three perovskites, and shift the equilibrium Fermi level towards the conduction band maximum, thus making the semiconductor conductivity more n-type. These substituents can not only help overcome the adverse effect of deep lying intrinsic defects, but their mid-gap energy provide an opportunity for sub-gap absorption which can potentially realize intermediate band solar cells[5]. Lastly, we performed correlation analysis on the computational data and discovered that the electronic and structural properties obtained from a much cheaper unit cell calculation can be used to reliably predict formation energies and transition levels of substitutional defects in lead halide perovskites. Such models can lead to accelerated prediction of impurity levels and allow efficient materials design of defect-tolerant perovskites as well as perovskites with suitably placed defect levels.

REFERENCES

10:45 AM ES15.05.04 Charge Carrier Trapping at Surface Defects and Optical Properties of Halide Perovskites Koichi Yamashita; Univ of Tokyo, Tokyo, Japan.

The high performance of recently emerged lead halide perovskite-based photovoltaic devices has been attributed to remarkable carrier properties in this kind of material: long carrier diffusion length, long carrier lifetime, and low electron-hole recombination rate. The charge carrier trapping at defects on surfaces or grain boundaries is detrimental for the performance of perovskite solar cells. In practice, it is one of the limiting factors for carrier lifetime. In my talk, I will discuss about surface defects responsible for carrier trapping and recombination according to first-principles investigations and it is proposed that PbI$_2$-rich condition is preferred to MAI-rich one, while intermediate condition has possibility to be the best choice [1]. On the other hand, in the continuous quest for better performing materials in photovoltaics and in view of their usage in optoelectronic devices, theoretical studies based on density functional and many-body perturbation theories on the electronic and optical properties of the mixed-valence CsAu$_4$I$_6$ fully inorganic double perovskite [2] and Ruddlesden–Popper organic–inorganic halide perovskites [3] will be discussed.

References

11:15 AM ES15.05.05 Spin Mixing Induced by Dynamical Disorder in Halide Perovskites Liang Z. Tan; Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

The Rashba effect has served as a model for the combined effects of spin-orbit coupling and inversion symmetry breaking in the halide perovskites. Simply interpreted, it is the splitting of spin components of parabolic energy bands, along directions perpendicular to a polar axis. However, the dynamical polar fluctuations of the halide perovskites suggest that they do not conform exactly to this simple model, because of the lack of a singular static polar axis. Computational simulations of the Rashba effect in the halide perovskites.
have often relied on either time-averaged or highly-selective crystal structures, and truncations of simulation cells, which do not accurately reflect the actual dynamics of halide perovskites.

In this work, we present a new model for spin-orbit effects in halide perovskites, treating the fluctuating crystal lattice as a disordered, spin-coupled medium. This model is described by spin transmission amplitudes and spin-flip amplitudes through this disordered medium. We parameterize our model on large-scale molecular dynamics trajectories, which captures the anharmonic, large-amplitude lattice fluctuations. Electronic structure calculations on these large simulation cells are aided by a tight-binding framework based on first-principles density functional theory calculations. We apply our model to carrier dynamics in halide perovskites, describing carrier mobility, relaxation, recombination, spin transport, and clarifying the role of spin-orbit coupling in these processes. Predictions of the temperature dependence of the carrier dynamics are given by this model, and compared with experimental results. We discuss the extent to which these effects on the optoelectronic properties may be interpreted as local and short-lived Rashba effects.

SESSION ES15.06: Spotlight Talks I: Fundamental Understanding of the Multifaceted Optoelectronic Properties of Halide Perovskites
Session Chairs: David Ginger and Samuel Stranks
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 130

11:30 AM ES15.06.01
Spotlight Talk—Impact of Flash Infrared Annealing on Growth and Photophysics of MAPbI3 Perovskite Loreta A. Muscarella1, Sandy Sanchez2, Andries Loi1, Michael Saliba1 and Bruno Ehrler1; 1FOM Institute AMOLF, Amsterdam, Netherlands; 2Adolphe Merkle Institute, Fribourg, Switzerland.

Flash Infrared Annealing (FIRA) results in pinhole free layers with micrometer size crystalline domains. The fast annealing times, and comparable solar cell efficiency compared to the traditional antisolvent fabricated perovskites make FIRA a highly promising method for the scaleup of perovskite solar cells. In this work we investigate how the Flash Infrared Annealing affects the crystal growth of MAPbI3 and its dependence on the substrates used. We measure the grain size, crystal structure and orientation using Electron Back-Scattered Diffraction (EBSD). We find a highly oriented cubic structure for perovskite annealed by FIRA and a consistent crystal rotation within perovskite grains. Besides, we study how the structural properties of the resulting films affect its photophysics. Combining photoluminescence lifetime and spectral maps we show how the growth method affects the steady-state and dynamic optical properties of the resulting films. Our findings directly relate structural properties to the photophysics of lead halide perovskites.

11:35 AM ES15.06.02
Spotlight Talk—Planar Perovskite Solar Cell by Two-Step Deposition Method via Blade-Coating Technique Zahra S. Almutawah, Ramez Hosseiniyan Ahanghamejhad, Zhaoning Song, Adam Phillips, Yantfa Yan and Michael Heben; University of Toledo, Toledo, Ohio, United States.

Organic-inorganic metal halide perovskites have attracted much interest and shown great promise in recent years due to their compatibility with cheap solution processing, ease of fabrication, and enhanced power conversion efficiencies. Currently, perovskite solar cells are transitioning from small area devices to large area devices that are compatible with manufacturing. Blade-coating is a promising deposition technique because it is a low cost, environmentally friendly, and easily translated to roll-to-roll processing. Most current work has focused on fabricating high efficiency perovskite solar cells using the single step-based blade coating. However, the most recent 23.3% record efficiency device was fabricated using the two-step spin-coating method. In this study, we investigate the possibility of fabricating large area perovskite solar cells by sequentially depositing PbI2 and mixed organic iodides consisting of FAI and MABr (where FA is formamidinium, and MA is methylammonium) using the blade coating technique. The blade-coated bi-layer precursor films are annealed under different conditions to examine conversion to the perovskite phases. This study will focus on understanding the formation and growth behaviors of perovskites formed in a two-step blade-coating process when the pre-deposited PbI2 films are reacted with various concentrations of mixed FA/MA cations. Comprehensive understanding of the nucleation and growth behavior of perovskites during the intercalation process will provide insights to improve control of the film quality and allow device performance for devices beyond the simple MAPbI3 system to be improved.

11:40 AM ES15.06.03
Spotlight Talk—Quantification of Ion Migration in MAPbBr3 Solar Cells with Varying Grain Size Lucie McGovern, Loreta A. Muscarella, Moritz H. Fuchscher and Bruno Ehrler; AMOLF, Amsterdam, Netherlands.

Hybrid halide perovskites have been attracting extensive interest as next generation photovoltaic technologies. Large bandgap metal halide perovskites such as MAPbBr3 offer a range of applications in multijunction solar cells, electrochemical energy storage, electrocatalysis, and LEDs, as well as providing an interesting platform for comparison with the more commonly studied MAPbI3, and mixed-halide perovskites.

It was shown that substituting Br for I increases the chemical stability making MAPbI3 solar cells more commonly studied MAPbI3 and its dependence on the substrates used. We measure the grain size, crystal structure and orientation using Electron Back-Scattered Diffraction (EBSD). We find a highly oriented cubic structure for perovskite annealed by FIRA and a consistent crystal rotation within perovskite grains. Besides, we study how the structural properties of the resulting films affect its photophysics. Combining photoluminescence lifetime and spectral maps we show how the growth method affects the steady-state and dynamic optical properties of the resulting films. Our findings directly relate structural properties to the photophysics of lead halide perovskites.

11:45 AM ES15.06.04
Spotlight Talk—Versatile Pseudo-Halide Based Perovskites—Photophysics and Utility in Optoelectronic Devices Satyawan Nagane1, Dibhayajoti Ghosh1, Wagnas Rehman1, Vijay Venugopalan1, Laura Herz2, Alison Walker1, Saiful Islam2, Satishchandra Ogale1 and Aditya Sadhanala1, 1Physics, University of Oxford, Oxford, United Kingdom; 2University of Cambridge, Cambridge, United Kingdom.

Pseudo-Halide have started to become a new stream of research because of their capability of not only replacing the scarce options of standard halides in perovskites (CI, Br and I), but also because of the unique and useful optoelectronic properties therein. This work will describe the versatility of using a organic pseudo halide based salt to fabricate various perovskites and demonstrate their resulting - interesting and unique photo-physical and optoelectronic properties.

11:50 AM ES15.06.05
Spotlight Talk—Control the Charge Accumulation for Efficient, Repeatable and Interface Stable Homo-Junction Planar Perovskite Solar Cells Jianxing Xia, Junsheng Luo, Fei Han, Zhongquan Wan, Yu Shi and Chongyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

The nature of trap defects such as the under-coordinated ions at the perovskite surface and grain boundaries are always trapping the free electrons or holes by the electrostatic force and speeding up the ion migration via the defect vacancy channels, which is significantly limiting the change extraction efficiency and devices long-term stability in perovskite solar cells. In this work, we induced an interface electric field which supplied by a molecular dipole to the interlayer of electron transfer layer (ETL) and perovskite. We employed Kelvin probe force microscope (KPFM) and Femtosecond transient absorption (fs-TA) to systematic study the states of charge distribution and transport properties in the perovskite after add the extra interface electric field. The results show a strong gradient electron accumulation at the applied interface and forming a homo-junction perovskite which supplied an extra built-in electric field (E_b), and finally resulting in faster interface charge transportation. Furthermore, the ion migration can efficiently be suppressed at the applied interface and thus reduce the disorder of energy level. Based on these results, we fabricated the PCBM based n-i-p architecture perovskite solar cell and achieving a PCE of 20.14% with high Voc of 1.14V, which is the record efficiency of PCBM based n-i-p devices. These devices also show higher stability compared to the standard cells.
Defect Physics and (In)Stability in Metal-Halide Perovskite Semiconductors

Defect Physics and (In)Stability in Metal-Halide Perovskite Semiconductors

SESSION ES15.07: Perovskite Composition and Defects Engineering II

Semiconducting metal-halide perovskites present various types of chemical interactions which give them a characteristic fluctuating structure sensitive to the operating conditions of the device, to which they adjust. This makes the control of structure-properties relationship, especially at interfaces where the device realizes its function, the crucial step in order to control devices operation. In particular, given their simple processability at relatively low temperature, one can expect an intrinsic level of structural/chemical disorder of the semiconductor which results in the formation of defects.

Here, first I will present our results on the role of structural and point defects in determining the nature and dynamic of photo-carriers in metal-halide perovskites. Then, I will discuss our understanding of key parameters which must be taken into consideration in order to evaluate the susceptibility of the perovskite crystals (2D and 3D) to the formation of defects, allowing one to proceed through a predictive synthetic procedure. Finally, I will show the correlation between the presence/formation of defects and the observed semiconductor instabilities. Instabilities are manifested as light-induced ion migration and segregation, eventually leading to material degradation under prolonged exposure to light. Understanding, controlling and eventually blocking such material instabilities are fundamental steps towards large scale exploitation of perovskite in optoelectronic devices.

2:00 PM ES15.07.02

Effect of Post-Deposition Annealing on Coevaporated CsPbBr3 Thin Films

Sebastian Caicedo Davila1, Jose Marquez Prieto1, Robert Lovrinovic2, Christian Müller1, Michael Sendner1, Thomas Unold1 and Daniel Abou-Ras1; 1Heinlernz-Zentrum Berlin, Berlin, Germany; 2InnovationLab GmbH, Heidelberg, Germany; 3Kirchhoff Institute of Physics, Universität Heidelberg, Heidelberg, Germany.

The all-inorganic cesium-lead-bromide perovskite (CsPbBr3) has attracted the attention of the photovoltaics community owing to its intrinsic thermal stability and high tolerance to humidity and light-induced effects [1–3]. Nevertheless, the coexistence of additional ternary phases (CsPbBr2 and CsPbBr3) in thin-films and single crystals [4], and its influence in the optoelectronic properties of the material is still a matter of debate and research [5]. Recent studies have shown that CsPbBr3 effectively passivates CsPbBr2 and reduces non-radiative recombination, which results in photodetectors and solar cells with outstanding performance [6,7]. Lei et al. reported enhancement of the photoluminescence and power conversion efficiency by controlled PbBr2 excess and high-temperature annealing of solar cells, synthesized by vacuum-thermal coevaporation of the CsPbBr3 absorber [3], while Luchkin et al. measured a significant current increase in coevaporated CsPbBr3 films after moderate-temperature thermal aging [8]. However, the mechanisms by which the optical and electrical properties are enhanced remain unclear.

In the present contribution, coevaporated CsPbBr3 films with excess PbBr2 on glass and Si substrates were studied. We probed the composition and optical properties of the surface and cross-section of the films by energy-dispersive X-ray (EDX) and cathodoluminescence (CL) spectroscopy, as well as by photoluminescence (PL) microscopy in a correlative analysis approach. The samples were investigated as-deposited and after (post-deposition) annealing at 70°C for 30 min in a N2 atmosphere. The EDX and CL cross-sectional analysis reveals that the temperature treatment increases the thickness of the CsPbBr3 layer in the film on Si substrate, while on the glass substrate the change is negligible. We estimate from absolute PL hyperspectral imaging an external PL quantum yield (PLQY) of 0.04% and quasi-Fermi-level splitting (QFLS) values exceeding 1.8 eV under one-sun equivalent conditions. Regardless of the thicker CsPbBr3 layer, we do not observe significant variations on the PLQY or QFLS after annealing. We discuss the effects of the substrate in the phase transformation and the influence of the phases on the optoelectronic properties of the films.


2:15 PM ES15.07.03

Improved Efficiency and Stability of Perovskite Solar Cells Induced by C=O Functionalized Hydrophobic Ammonium-Based Additives

Zhiyang Wu and Yabing Qi; Okinawa Institute of Science and Technology, Okinawa, Japan.

Organic-inorganic hybrid perovskite solar cells show the promises as the next-generation photovoltaic technology. The efficiency has quickly increased from 3.8% [1] to 23.2% since 2009 [2]. The morphology and crystal quality of perovskite films are the critical factors affecting solar cell efficiency. Here we introduce a new organic ammonium additive (2-NAM), exhibiting strong Lewis acid-base interaction with perovskite. [3] 2-NAM is expected to retard the kinetics for crystal growth instead of generating multiple nucleation points, finally resulting in larger crystal grain sizes. In addition, 2-NAM effectively passivates defect formed by the uncoordinated Pb atom. As result, the number of defects decreases almost three times. After introducing 2-NAM, efficiency increases from the 17.1 ± 0.8% to 18.6 ± 0.9% for 0.1 cm2 cell and 15.5 ± 0.5% to 16.5 ± 0.6% for 1.0 cm2 cell, respectively. Besides the improved efficiency, the stability is enhanced.

2:30 PM BREAK

SESSION ES15.08: First Principles and Computational Screening II

3:30 PM ES15.08.01

Atomistic Origins of Carrier Recombination in Grain Boundaries of Halide Perovskites

Ji-Sang Park and Aron Walsh; Imperial College London, London, United Kingdom.
Hybrid inorganic-organic perovskite solar cells have attracted much attention because of their superior materials properties, inexpensive fabrication methods, and their rapidly increasing solar conversion efficiency from 3.8% to more than 22% within 10 years. To further improve the solar conversion efficiency, all aspects of the device should be comprehensively analyzed at the fundamental level [1]. One problem not completely answered is whether the grain boundaries in halide perovskites are detrimental and which atomic feature makes the grain boundaries have such properties. Density functional theory (DFT) calculation studies claim that grain boundaries do not have gap states [2-3], whereas another group claimed that the lifetime can be reduced on the interface dynamics simulations [4]. Our investigation of extended defects in other materials (e.g., CdTe) shows that grain boundaries can be non-stoichiometric depending on the growth conditions [5,6], indicating that grain boundaries in halide perovskites are likely non-stoichiometric due to segregation of intrinsic or extrinsic defects. In this presentation, we aim to discuss the stability and electrical properties of grain boundaries in halide perovskites in comparison to CdTe and provide a clue to passivate grain boundaries in general.


3:45 PM ES15.08.02
Long-Range FRET-Mediated Exciton Diffusion in Cesium Lead Halide Perovskite Nanosstructures

Monica Lorenzon1, Anna Loido1, Edward K. Wong1, Matthew Jurove1, Min Ji Hong1, Yi-Hsien Lua1,2, Edward K. Wong1, Miquel Salmonero1, Yi Liu1,2, Stefano Cabrin1, Stephen Whitelam1, Raffaella Buonsanti1, Adam M. Schwartzberg1, Erika Penzo2 and Alexander Weber-Bargioni1
1The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Department of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Sion, Switzerland.

Colloidal inorganic perovskite nanocrystals (PNCs) are solution-processable functional materials whose emission can be easily tuned via both size and composition. 1 Their exciting optical properties such as the large absorption cross-section and high photoluminescence quantum yield (PLQY) make them ideal candidates for a broad range of photonics and optoelectronics applications. 2 In this work, we present an overview of the exceptionally efficient exciton transport mediated by Förster Resonant Energy Transfer (FRET) in perovskite systems of increasing dimensionality. With a specifically designated optical setup, we directly measure the spatial extent of exciton hopping in a controlled two-dimensional assembly of 0D PNCs, which provides a flat energy landscape with minimal geometric disorder. 3 Steady-state and time-resolved PL microscopy, together with physical modeling of exciton transport, shows an exciton diffusion length of 200 nm and diffusivity as high as 0.5 cm2/s, which greatly exceed the values reported for FRET-mediated exciton diffusion in chalcogen-based quantum dot solids, and, importantly, matches the optical absorption depth. We further explore the exciton diffusion paradigm in 1D perovskite nanowires and 2D nanosheets, where we image the diffusion across the whole system, with diffusion lengths larger than 1µm. In addition to the exciton diffusion mapping, a significant portion of this work has been dedicated to the optimization of the substrate and the sample passivation. Specifically, we show that with a thermal-based atomic layer deposition process we are able to apply a ~3nm-thick transparent ceramic coating (aluminum oxide) which ensure optical stability over a four month period, thus overcoming the instability issue which often hinders the actual integration of perovskite materials in optoelectronic devices. Our investigation therefore provides the foundation for employing FRET-mediated exciton diffusion in nanostructured perovskites, while also demonstrating practical guidelines to use these bright emitters in optoelectronic devices beyond proof of principle.

References

4:00 PM ES15.08.03
Structural Disordering and Inversion Symmetry Breaking in Layered Hybrid Perovskite Halides

Wei Xie1, Mark Asta and Matthew Sherburne1; Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Layered hybrid perovskite halides are under intense investigation for electronic, optoelectronic, dielectric and photovoltaic applications due to advantages in stability, diversity, tunability and solution synthesizability. We reveal, through first-principles calculations how structural disordering and inversion symmetry breaking adapt as functions of composition and topological dimensionality of the octahedral net (controlled by the number of perovskite layers n) in a prototypical series of hybrid Ruddlesden-Popper halides PnAmpn-1MxAmpn-1Brn. We perform density functional theory (DFT) calculations of these phenomena as the complex interplay of Pb-X covalent bonding, hydrogen bonding between ammonium head of PEA and apical halides, and van der Waals interactions between the aromatic tails of PEA. Our investigation therefore provides the foundation for employing FRET-mediated exciton diffusion in nanostructured perovskites, while also demonstrating practical guidelines to use these bright emitters in optoelectronic devices beyond proof of principle.

References

4:15 PM ES15.08.04
Rashba-Dresselhaus Triggered Electronic and Optical Properties in De Novo Designed Mixed Halide Hybrid Perovskites—Implication of Composition Route and Stoichiometry

Amitava Banerjee1, Sudip Chakraborty and Rajeev Ahuja2;Upsala University, Uppsala, Sweden.

The structural peculiarities in hybrid perovskites (ABX3, where A=organic cation, B=metal, X=halide) often lead to a wide range of exciting electronic and optical properties with a consequent effect on the efficiency and stability of the optoelectronic devices based on these materials. The Rashba-Dresselhaus effect is one such consequence that has prevailed in the hybrid perovskite family. The inherent spin-orbit coupling (SOC) effect in a non-centrosymmetric crystal structure of hybrid perovskite systems has laid the foundation of Rashba-Dresselhaus effect. This Rashba-Dresselhaus effect is spin splitting of the charge carrier recombination, which eventually controls the carrier lifetime and diffusion length and therefore the solar cell efficiency for such hybrid perovskite materials. In this work, we depict a vivid picture of Rashba-Dresselhaus effect in hybrid perovskites and the immediate implications in the field of optoelectronics. Here we have performed a rigorous structural search prediction of the mixed cation-mixed halide hybrid perovskites FA0.85MA0.15(PbI2.83Br0.17)3 and FA0.85MA0.15(PbI2.83Br0.17)3 which are the two nearest neighbor structure of record efficiency (22.1%) holder FA0.85MA0.15(PbI2.83Br0.17)3 in the structural composition phase-space. We have found the prediction routes for such structural search as the mixed perovskite structure govern the Rashba-Dresselhaus splitting energy value, depending on whether it is predicted from FPI or MBP as parent structure, which is leading to the mixed phase FA0.85MA0.15(PbI2.83Br0.17)3 and FA0.85MA0.15(PbI2.83Br0.17)3 respectively. The strong dependency of the splitting energy on the structural phase evolution along with the stoichiometry and space-group is also observed, wherein the mixed phase, 0.045 difference in concentration could lead to a remarkable difference in the splitting energy, which is more pronounced in the valence band as compared to the conduction band. We have also determined the Goldschmidt tolerance factor to envisage structural stability of the newly predicted crystal structure from both the chemical route in the composition phase space.
_cells based on Methyl-Ammnonium Lead Triiodide (MAPbI3) perovskite have gained attention due to their remarkable progress in performance efficiency during recent years [1]. However, it has been hampered to put the material on the market due to their device stability under exposure to moisture [2] which is one of the major obstacle toward outdoor application of photovoltaic devices. A comprehensive study on degradation mechanism initiated with water molecules is thus essential for practical realization of MAPbI3 based solar cells. Using first-principles calculation based on the density-functional theory, we here focus on and investigate ion-migration dynamics in a MAPbI3 intercalated with water and their enhancement by the influence of grain boundary (GB). The nudged elastic band (NEB) method is employed to find the barrier potential and corresponding optimal minimum energy path (MEP) of migrated ions. We find that one of H ions of a water molecule segregated into a GB is dissociated, migrated along the GB, and attracted by an N atom in the MAPbI3 with comparatively lower potential barrier (~0.27eV) [3], following the H-ion release from an ammonium. Such migration of H depends upon the subsequent changes of charge states of surrounding atoms [4]. Additionally, a vacant space around the N atom plays as a cage for the diffused H atom. The water intercalation greatly reduces the barrier potential for an H ion motion in the GB interior of MAPbI3 which can be liable to initiate the degradation of crystallinity of the perovskite. The iso-surface of electronic charge distribution at HOMO-LUMO and partial density of state (PDOS) of the ruling N atom reveal the mentioned phenomenon. More importantly, the anisotropy symmetric GB structure is prominent for faster molecular attractions due to their weak activation energies.

*Work supported by the JSPS KAKENHI Grant Number 18H01708

References:

Spotlight Talk—First-Principles Study on Water Dissociation in Grain Boundary of MAPbI3 Perovskite

Hybrid organic-inorganic perovskite solar cell (PSC) has been paid much attention due to its rapid progress of power conversion efficiency exceeding 22%. Many methods for preparing the perovskite films have been proposed, such as one-step deposition, sequential deposition, vapor-assisted deposition, and so on. Among them, the sequential deposition, typically synthesized by the immersion of PbI2 into the MAI solution to form the MAPbI3 perovskite film, shows the promise because of its better control over the surface morphology and crystallization kinetics. However, the incomplete conversion during sequential deposition, resulting in the residue of PbI2 left, becomes the problem and thereby influences the device performance reproducibly. In this regard, we introduce a vacuum treatment to treat the samples at the different stages of the sequentially deposition to investigate the level of PbI2 left. The SEM and XRD are used to identify the morphology, the crystallization and the conversion of the perovskite film during the sequential deposition. Our result indicates that the as-prepared PbI3 forms a compact morphology after the vacuum treatment, leading to more amount of PbI3 left within the resulting perovskite film. On the other hand, the vacuum treatment is applied for the PbI2 film right after the MAI immersion, showing a less amount of PbI2 left within the resulting perovskite film. The UV-Vis and EIS are carried out to analyze the optical property and charge transport property, respectively, of perovskite films with different level of PbI2 residue. J-V characteristic of the perovskite solar cells with the different level of PbI2 residue is tested under AM 1.5G illumination. More details of the conversion efficiency of perovskite solar cells, affected by vacuum treatment at the different stages of sequential deposition, will be discussed in the presentation.

4:45 PM ES15.09.04

Spotlight Talk—Analysis of Charge Transfer Dynamics in Planar and Mesoporous Mixed Halide Perovskite Solar Cells

For photovoltaic devices based on hybrid organic-inorganic perovskites thin films has remained elusive. Herein, we have analyzed the influence of chloride substitution on interfacial charge transfer dynamics in perovskite thin films with two different architectures. We compare different mixed MAPbI3 perovskite films fabricated under identical conditions that differ only in the TiO2 residue is tested under AM 1.5G illumination. More details of the conversion efficiency of perovskite solar cells, affected by vacuum treatment at the different stages of sequential deposition, will be discussed in the presentation.

4:50 PM ES15.09.05

Spotlight Talk—Conductivity Tuning via Doping with Electron Donating and Withdrawing Molecules in Perovskite CsPbX3 Nanocrystal Films

Doping of semiconductors allows tunability of charge carriers and subsequently electronic properties necessary for the development of many technologies. However, controlled doping in lead-halide perovskite semiconductors has proven to be difficult. Lower dimensional perovskites such as nanocrystals, with their high surface area to volume ratio, offer an opportunity for electronic doping via molecular charge transfer. In our work, we explore the tunability of the electronic properties of perovskite nanocrystal films using...
physically adsorbed molecular dopants. Incorporation of the dopant molecules into CsPbI$_3$ nanocrystal thin films is confirmed via infrared and photoelectron spectroscopies. We discover pre-treated CsPbI$_3$ nanocrystal films to be slightly p-type in behavior. Incorporating an electron-accepting dopant increases conductivity while an electron-donating molecule results in lower conductivity, appearing to compensate the p-type nanocrystal arrays. Time-resolved spectroscopic measurements reveal time scales on the order of August-mediated recombination in the presence of excess electrons or holes. Transport measurements demonstrate that both the local and long-range hole mobility is improved by doping of the nanocrystal arrays using an electron-accepting molecule. The improved photo-excited hole mobility in p-type arrays lead to an enhancement in photo-transistors.

SESSION ES15.10: Poster Session
Session Chairs: Luis Ono and Yabing Qi
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES15.10.01
Spotlight Talk—Analysis of Charge Transfer Dynamics in Planar and Mesoporous Mixed Halide Perovskite Solar Cells Zhongguo Li,$^{1,2}$ and Clemens Burda$^{3}$; $^{1}$College of Physics and Electronic Engineering, Changshu Institute of Technology, Suzhou, China; $^{2}$Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, United States.

For photovoltaic devices based on hybrid organic-inorganic perovskites thin films, the cell architecture is a vital parameter in defining the macroscopic performance. To date, there are a handful of studies about the carrier dynamics in perovskite devices with various morphologies. However, the correlation between architecture and carrier dynamics in mixed perovskites thin films has remained elusive. Herein, we have analyzed the influence of chloride substitution on interfacial charge transfer dynamics in perovskite thin films with two different architectures. We compare different mixed MAPbI$_3$ solar cells fabricated under identical conditions that differ only in the TiO$_2$ layer, therefore decouple the composition impact from device performance. Our results clearly demonstrate that the enhancement mechanism of power conversion efficiency is dramatically different in planar and mesoscopic architectures. In planar architecture, Cl substitution leads to faster electron injection rate from perovskite to planar TiO$_2$. In contrast, Cl addition demonstrate no discernable influence on electron injection to mesoporous TiO$_2$, suggesting the retarded interfacial charge recombination give rise to improved performance. This result could be useful for future photovoltaic and optoelectrical devices based on halide perovskite.

ES15.10.02
Spotlight Talk—The Study of PbI$_2$ Residues in Sequential Deposition Syue-Yi Jhan, Jian-Hua Wang and Chuh-Liang Wang; Graduate Institute of Precision Engineering, National Chung Hsing University, Taichung City, Taiwan.

Hybrid organic-inorganic perovskite solar cell (PSC) has been paid much attention due to its rapid progress of power conversion efficiency exceeding 22%. Many methods for preparing the perovskite films have been proposed, such as one-step deposition, sequential deposition, vapor-assisted deposition, and so on. Among them, the sequential deposition, typically synthesized by the immersion of PbI$_2$ into the MAI solution to form the MAPbI$_3$ perovskite film, shows the promise because of its better control over the surface morphology and crystalization kinetics. However, the incomplete conversion during sequential deposition, resulting in the residue of PbI$_2$, leads to the problem and thereby influences the device performance reproducibly. In this regard, we introduce a vacuum treatment to treat the samples at the different stages of the sequential deposition to investigate the level of PbI$_2$ left. The SEM and XRD are used to identify the morphology, the crystallization and the conversion of the perovskite film during the sequential deposition. Our result indicates that the as-prepared PbI$_2$ forms a compact morphology after the vacuum treatment, leading to more amount of PbI$_2$ left within the resulting perovskite film. On the other hand, the vacuum treatment is applied for the PbI$_2$ film right after the MAI immersion, showing a less amount of PbI$_2$ left within the resulting perovskite film. The UV-Vis and EIS are carried out to analyze the optical property and charge transport property, respectively, of perovskite films with different level of PbI$_2$ residue. J-V characteristic of the perovskite solar cells with different level of PbI$_2$ residue is tested under AM 1.5G illumination. More details of the conversion efficiency of perovskite solar cells, affected by vacuum treatment at the different stages of sequential deposition, will be discussed in the presentation.

ES15.10.03
General Strategy for Defects Passivation in Crystalline Organo-Metal Halide Perovskite Film to Enhance Its Photovoltaic Performance and Stability Kai-Chi Hsiao, Bo-Ting Lee and Wei-Fang W. Su; National Taiwan University, Taipei City, Taiwan.

Outstanding power conversion efficiency of organo-metal halide perovskite solar cell loses its open-circuit voltage (Voc) and stability in ambient environment. Understanding the underlying mechanisms of instability and Voc loss are urgently needed to resolve the issues. Ionic defects (anion and cation vacancies) in perovskite, especially in mixed cation and halide perovskite, are regarded as the major factor to deteriorate the stability and efficiency. Suppress ionic defects can directly retard both trapped-assist recombination of charge carriers and the diffusion of gas molecules (i.e. moisture, oxygen) in perovskite and therefore improve the Voc and stability of device.

Herein, we report a general strategy of post-treatment using Lewis adduct to passivate ionic vacancies in crystalline perovskite film to improve its device performance and stability. The Lewis adducts of organo ammonium salt were investigated. The systematical characterizations of passivated films reveal the electronic disorder and trapped density are successfully reduced after Lewis adduct post-treatment. A more than 50 mV increase in Voc has been achieved due to the less non-radiative recombination of charge carriers as compared with the device without passivation. In term of device stability, less than 1% power conversion efficiency was observed when the device was irradiated 10 min continuously and the 300-second maximum power point was tracked simultaneously in the ambient. Compared with conventional passivation approaches which are carried out at the crystallization step of perovskite film and are difficult to control, this strategy can directly passivate the ionic defects after the film is crystallized. That gives an avenue to the ultrafast or one-step large-scale coating process to obtain a high-quality perovskite film with ease which has potential to become a commercial viable process.

ES15.10.04
Spotlight Talk—Vapor Growth of In-Plane Directional CsPbX$_3$ Perovskite Nanowires for High-Performance Photonics and Optoelectronic Devices Weihao Zheng, Muhammad Shoaib, Xiaoxia Wang and Anlian Pan; Hunan University, Changsha, China.

Recently, all-inorganic perovskites CsPbX$_3$ (X = Cl, Br, I) nanowires (NWs) have recently demonstrated potential applications in integrated photonics devices such as lasers and photodetectors due to their unique physical and chemical characteristics. Considering the perovskite based integration application, large-scale growth or assembly of perovskite nanowires with horizontal alignment on surfaces is highly desirable. Here, we demonstrate the controlled growth of in-plane directional perovskite CsPbBr$_3$ NWs, induced by graphoepitaxial effect on annealed M-plane sapphire substrates. High-performance photodetectors constructed on these individual NWs exhibit excellent photoresponse with an ultrahigh responsivity of 4400 A/W and fast response speed of 252 μs. Furthermore, we achieved wavelength-tunable CsPbX$_3$ nanowire laser arrays at room temperature with quite low lasing thresholds and high quality factors based on the directional growth approach. Meanwhile, we studied the exciton–photon coupling effect of these perovskite nanowire cavities under the excitation of a pulsed laser, from which highly atomic composition dependent Rabi splitting of ~210 ± 13, 146 ± 9, and 103 ± 5 meV for the CsPbCl$_3$, CsPbBr$_3$, and CsPbI$_3$ are obtained at room temperature. In addition, by using a novel temperature difference triggers growth strategy, high quality CsPbX$_3$ nanowire arrays with the integration of the merits of the liquid- and gas-phase methods was successfully synthesized, these nanowire arrays show excellent stability and good optoelectronic properties at room temperature. This work presents an important step toward scalable growth of high-quality perovskite NWs, which will provide promising opportunities in constructing integrated nanophotonic and optoelectronic systems.

References:

ES15.10.05
Solar cells based on Methyl-Ammonium Lead Triiodide (MAPbI3) perovskite have gained attention due to their remarkable progress in performance efficiency during recent years [1]. However, it has been hampered to put the material on the market due to their device stability under outdoor application of photovoltaic devices. A comprehensive study on degradation mechanism initiated with water molecules is thus essential for practical realization of MAPbI3 based solar cells. Using first-principles calculation based on the density-functional theory, we here focus on and investigate ion-migration dynamics in a MAPbI3 intercalated with water and their enhancement by the influence of grain boundary (GB). The nudged elastic band (NEB) method is employed to find the barrier potential and corresponding optimal minimum energy path (MEP) of migrated ions. We find that one of H ions of a water molecule segregated into a GB is dissociated, migrated along the GB, and attracted by an N atom in the MAPbI3 with comparatively lower potential barrier (~0.27eV) [3], following the H-ion release from an ammonium. Such migration of H depends upon the subsequent changes of charge states of surrounding atoms [4]. Additionally, a vacant space around the N atom plays as a cage for the diffused H atom. The water intercalation greatly reduces the barrier potential for an H-ion motion in the GB interior of MAPbI3 which can be liable to initiate the degradation of crystallinity of the perovskite. The iso-surface of electronic charge distribution at HOMO-LUMO and partial density of state (PDOS) of the ruling N atom reveal the mentioned phenomenon. More importantly, the antisymmetric GB structure is prominent for faster molecular attractions due to their weak activation energies.

*Work supported by the JSPS KAKENHI Grant Number 18H01708

References:

ES15.10.06 Spotlight Talk—Control the Charge Accumulation for Efficient, Repeatable and Interface Stable Homo-Junction Planar Perovskite Solar Cells Jianxing Xia, Junsheng Luo, Fei Han, Zhongquan Wan, Yu Shi and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

The nature of trap defects such as the under-coordinated ions at the perovskite surface and grain boundaries are always trapping the free electrons or holes by the electrostatic force and speeding up the ion migration via the defect vacancy channels, which is significantly limiting the charge extraction efficiency and devices long-term stability in perovskite solar cells. In this work, we induced an external electric field which supplied by a molecular dipole to the interlayer of electron transfer layer (ETL) and perovskite. We employed Kelvin probe force microscope (KPFM) and Femtosecond transient absorption (fs-TA) to systematic study the states of charge distribution and transport properties in the perovskite after add the extra interface electric field. The results show a strong gradient electron accumulation at the applied interface and forming a homo-junction perovskite which supplied an extra built-in electric field (E_B), and finally resulting in faster interface charge transportation. Furthermore, the ion migration can efficiently be suppressed at the applied interface and thus reduce the disorder of energy level. Based on these results, we fabricated the PC61BM based n-i-p architecture perovskite solar cell and achieving a PCE of 20.14% with high Voc of 1.14V, which is the record efficiency of PC61BM based n-i-p devices. These devices also show higher stability compared to the standard cells.

ES15.10.07 Spotlight Talk—Versatile Pseudo-Halide Based Perovskites—Photophysics and Utility in Optoelectronic Devices Satyawan Nagane, Dhabyajoti Ghosh, Wagaas Rehman, Vijay Venugopala, Laura Herz, Alison Walker, Saiful Islam, Satishchandra Ogale and Aditya Sadhanala; 1) University of Cambridge, Cambridge, United Kingdom; 2) Physics, University of Oxford, Oxford, United Kingdom; 3) University of Bath, Bath, United Kingdom; and 4) Indian Institute of Science Education and Research, Pune, India.

Pseudo-Halide have started to become a new stream of research because of their capability of not only replacing the scarce options of standard halides in perovskites (Cl, Br and I), but also because of the unique and useful optoelectronic properties therein. This work will describe the versatility of using a organo pseudo halide based salt to fabricate various perovskites and demonstrate their resulting - interesting and unique photo-physical and optoelectronic properties.

ES15.10.08 Spotlight Talk—Quantification of Ion Migration in MAPbBr3 Solar Cells with Varying Grain Size Lucie McGovern, Loreta A. Muscarella, Moritz H. Fuchscher and Bruno Ehrler; AMOLF, Amsterdam, Netherlands.

Hybrid halide perovskites have been attracting extensive interest as next generation photovoltaic technologies. Large bandgap metal halide perovskites such as MAPbBr3 offer a range of applications in multijunction solar cells, electrochemical energy storage, electrocatalysis, and LEDs, as well as providing an interesting platform for comparison with the more commonly studied MAPbI3, and mixed-halide perovskites.

It was shown that substituting Br for I increases the chemical stability making MAPbBr3 much more stable under environmental conditions when compared to MAPbI3. We study this increase in stability under environmental conditions and show that it stems from a change in ion migration properties when going from MAPbI3 to MAPbBr3. Furthermore, we investigate the evolution of this behavior in different MAPbBr3 solar cells as a function of the grain size of the active perovskite film. Grain boundaries change ion migration by providing alternative pathways for the ions to migrate, thereby affecting crucial properties of the process such as activation energy and diffusion coefficient. In our work, we use Transient Ion Drift to quantify the activation energies, diffusion coefficients, and concentrations of the mobile ions, and show the link between grain size, ion migration, and stability.

ES15.10.09 Spotlight Talk—Planar Perovskite Solar Cell by Two-Step Deposition Method via Blade-Coating Technique Zahrah S. Almutawah, Ramez Hosseinian Ahangharnajad, Zhaoning Song, Adam Phillips, Yanfa Yan and Michael Heben; University of Toledo, Toledo, Ohio, United States.

Organic-inorganic metal halide perovskites have attracted much interest and shown great promise in recent years due to their compatibility with cheap solution processing, ease of fabrication, and enhanced power conversion efficiencies. Currently, perovskite solar cells are transitioning from small area devices to large area devices that are compatible with manufacturing. Blade-coating is a promising deposition technique because it is a low cost, environmentally friendly, and easily translated to roll-to-roll processing. Most current work has ever been focused on the advantages of high efficiencies for perovskite solar cells using the single-step blade coating. However, the most recent 23.3% record efficiency device was fabricated using the two-step spin-coating method. In this study, we investigate the possibility of fabricating large area perovskite solar cells by sequentially depositing PbI3 and mixed organic iodides consisting of FAI and MABr (where FA is formamidinium, and MA is methylammonium) using the blade coating technique. The blade-coated bi-layer precursor films are annealed under different conditions to examine the perovskite phases. This study will focus on understanding the formation and growth behaviors of perovskites formed in a two-step blade-coating process when the pre-deposited PbI3 films are reacted with organic iodide solution with various concentrations of mixed FA/MA cations. Comprehensive understanding of the nucleation and growth behavior of perovskites during the intercalation process will provide insights to improve control of the film quality and allow device performance for devices beyond the simple MAPbI3 system to be improved.

ES15.10.10 Spotlight Talk—Impact of Flash Infrared Annealing on Growth and Photodynamics of MAPbI3 Perovskite Loreta A. Muscarella, Sandy Sanchez, Andries Lof, Michael Saliba and Bruno Ehrler; FOM Institute AMOLF, Amsterdam, Netherlands; Adolphe Merkle Institute, Fribourg, Switzerland.

Flash Infrared Annealing (FIRA) results in pinhole free layers with micrometer size crystalline domains. The fast annealing times, and comparable solar cell efficiency compared to the traditional antisolvent fabricated perovskite solar cells make FIRA a highly promising method for the scaleup of perovskite solar cells. In this work we investigate how the Flash Infrared Annealing affects the crystal growth of MAPbI3 and its dependence on the substrates used. We measure the grain size, crystal structure and orientation using Electron Back-Scattered Diffraction (EBSD). We find a highly oriented cubic structure for perovskite annealed by FIRA and a consistent crystal rotation within perovskite grains. Besides,
we study how the structural properties of the resulting films affect its photophysics. Combining photoluminescence lifetime and spectral maps we show how the growth method affects the steady-state and dynamic optical properties of the resulting films. Our findings directly relate structural properties to the photophysics of lead halide perovskites.

ES15.10.11
Spotlight Talk—Conductivity Tuning via Doping with Electron Donating and Withdrawing Molecules in Perovskite CsPbI$_2$ Nanocrystal Films Ashley Gaulding1, Ji Hao1, Hyun Suk Kang1, Elisa Miller1, Severin N. Habriseutinger1, Qian Zhao1,2, Abhijit Hazarika1, Joseph Luther2 and Jeffrey Blackburn3; 1National Renewable Energy Lab, Golden, Colorado, United States; 2Nankai University, Tianjin, China.

Doping of semiconductors allows tunability of charge carriers and subsequently electronic properties necessary for the development of many technologies. However, controlled doping in lead-halide perovskite semiconductors has proven to be difficult. Lower dimensional perovskites such as nanocrystals, with their high surface area to volume ratio, offer an opportunity for electronic doping via molecular charge transfer. In our work, we explore the tunability of the electronic properties of perovskite nanocrystal films using physically adsorbed molecular dopants. Incorporation of the dopant molecules into CsPbI$_2$ nanocrystal thin films is confirmed via infrared and photoelectron spectroscopies. We discover pre-treated CsPbI$_2$ nanocrystal films to be slightly p-type in behavior. Incorporating an electron-accepting dopant increases conductivity while an electron-donating molecule results in lower conductivity, appearing to compensate the p-type nanocrystal arrays. Time-resolved spectroscopic measurements reveal time scales on the order of Auger-mediated recombination in the presence of excess electrons or holes. Transport measurements demonstrate that both the local and long-range hole mobility is improved by doping of the nanocrystal arrays using an electron-accepting molecule. The improved photo-excited hole mobility in p-type arrays lead to an enhancement in photo-transistors.

ES15.10.12
Hot Carrier Dynamics in Lead Halide Perovskites from a THz Mobility Perspective Andrés Burgos-Caminal, Aurélien Willauer, Ahmad Ajdar Zadeh and Jacques-E. Moser; Photophysical Dynamics Group, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland.

Ultrafast time-resolved terahertz spectroscopy (TRTS) allows for the direct probing of charge carriers and quasi-particles in semiconductors. The sensitivity of the technique to both the carrier mobility and its density can help elucidate the mechanisms of their temporal evolution. The use of gas photodetectors provides short, ultra-broadband THz pulses and, thus, offers an improved time-resolution.

Here, we present a study of the early stages of the charge carrier dynamics in lead halide perovskite thin films from the point of view of the THz mobility. Taking advantage of a 200 fs time-resolution, we were able to temporally follow the cooling of hot carriers through the observation of the change of the carrier's mobility. This change is understood as resulting from a modification of the effective mass.1

Our results are compatible with a hot carrier cooling mechanism implying LO phonon emission. This is subjected to a phonon bottleneck, and competes with a dynamic screening process, which time-constant is identified as being due to polaron formation.3 While the screened hot carriers take longer to cool down, the dynamic screening process does not produce a change in mobility when only cold carriers are involved.

Measurements applied to perovskite samples of various compositions are compared to elucidate the role of cations and anions in both processes.


SESSION ES15.11 Interface Physics and Charge Extraction
Session Chair: Sanford Ruhan
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 130

8:00 AM ★ES15.11.01 Interfaces Halide Perovskites: Passivating Defects for Reduced Non-Radiative Recombination David S. Ginger; University of Washington, Seattle, Washington, United States.

In this talk we describe the role of interfaces and surface defects on non-radiative recombination losses in hybrid perovskite semiconductors. Using combinations of microscopy and time-resolved photoluminescence spectroscopy we show that not only are perovskite surfaces sources of significant non-radiative loss, but that chemical passivation of surface states can lead to near-ideal semiconductor properties, achieving over 90% PL internal quantum efficiency and quasi-Fermi level splittings that exceed 96% of the Shockley-Queisser limit under illumination. We next explore the interface between the perovskite and various charge extraction layers, combining experiment and simulation to show that surface recombination at the charge extraction layers is a limitation in current perovskite solar cell architectures.

8:30 AM ★ES15.11.02 Interface Energetics of Halide Perovskites Philip Schulz; CNRS-Institut Photovoltaique d'Ile de France (IPVF), Palaiseau, France.

My talk will focus on the means and developments to analyze and tailor interfaces in halide perovskite (Hp) based semiconductor devices to gain control over the electronic properties at the nanoscale, as interfacial design routes determine the electronic coupling between the perovskite absorber and adjacent charge extraction and transport layers. On the one hand, the device characteristics can be affected by the alignment of the frontier molecular orbitals of an organic charge transport layers (CTL) with the electronic transport level in the perovskite. On the other hand, the doping type of the substrate underneath can template the doping type of subsequently deposited Hp films. In our studies we elucidated these mechanisms by examining a selection of organic, oxide and carbon nanotube charge transport layers adjacent to the perovskite film [1].

In my talk, I will highlight the use of ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) as well as inverse photoemission spectroscopy (IPES) to determine the surface energetics and electronic energy level alignment at the MHP/CTL interface while at the same time tracking the interface chemistry. This approach enables us to explain band offset in the perovskite layer by either chemical interactions or by changes in the electrostatic potential. The results not only suggest guidelines on how to integrate charge extraction layers into perovskite photovoltaic devices but also explain more generally what to expect when the electronic structure of the perovskite is subject to extrinsic perturbations [2].

I will conclude my talk by further demonstrate the impact of surface treatment and interfacial design routes to the achievement of record power conversion efficiencies in Hp-based quantum dot solar cells [3]. Therein, our approach is driven by a targeted ligand exchange chemistry that results in subsequent anion and cation exchange reactions at the quantum dot surface [4].


9:00 AM ★ES15.11.03 Electronic Properties at Surfaces of n= 1 and 2 Ruddlesden-Popper Phase Perovskites Scott Silver1, Hong Li2, Jean-Luc Bredas2 and Antoine Kahn1; 1Department of Electrical Engineering, Princeton University, Princeton, New Jersey, United States; 2School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia, United States.

Increasing attention has been placed over the past few years on 2D Ruddlesden-Popper phase (RPP) metal halides, perceived as interesting photovoltaic materials in their own right, and also as potentially efficient capping materials to improve the long-term stability of 3D metal halide perovskite solar cells. Energy level alignment at 2D/3D
heterojunctions and stability of the 2D materials are therefore of considerable interest. We focus here on the electronic surface, surface potential and response to light irradiation of films of the 2D RPP metal halides, Ba$_2$PbI$_4$ (n=1) and Ba$_2$Ca$_2$Pb$_3$I$_7$ (n=2). Direct and inverse photoemission spectroscopy coupled with theoretical computation of the DOS are used to determine the materials electron affinity (EA)/ionization energy (IE), equal to 3.1.5.8 eV for Ba$_2$PbI$_4$ [1] and 3.3.5.7 eV for Ba$_2$Ca$_2$Pb$_3$I$_7$. A full identification of the various contribution to the valence and conduction band DOS is made. We investigate the surface potential of these films via Kelvin probe force microscopy and show reproducible surface photovoltage under supra-band gap light irradiation, corresponding to a reduction of the downward band bending. Long term degradation of the work function is not observed, in contrast to previous observations on 3D perovskite surfaces. Finally, a composition analysis of the n=2 Ba$_2$Ca$_2$Pb$_3$I$_7$ using XPS, shows that the surface is not stoichiometric and resembles the composition of RPPs with larger n. We propose that the n=2 phases at the surface create a type I interface with the n=2 phase. This information together with the IE and EA as determined by UPS and IPES, respectively, outline the energy landscape of this material.


9:30 AM ES15.11.04

Spiro-MeOTAD Hole Transport Material in Perovskite-Based Solar Cells


In halide perovskite-based solar cells, optimization of hole transport materials (HTMs) is important for enhancing solar power conversion efficiency and stability [1, 2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit has been making concerted efforts to study 2.2',7',7''-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobi fluorenone (spiro-MeOTAD), which is the most widely used HTM in perovskite solar cells [2,9]. In this talk, we will present our latest understanding of fundamental interactions between Li-bis(trifluoromethanesulfonyl)-imide (LiTFSI), tert-butylpyridine (t-BP), spiro-MeOTAD and perovskites. Also, we will show how gas exposure (e.g., exposure to O$_2$, H$_2$O, N$_2$) influences electronic energy level alignments and conductivity of such HTM films that is closely associated with performances and stability in perovskite-based solar cells.


9:45 AM ES15.11.05

Effect of Ligand Groups on Photoexcited Charge Carrier Dynamics at Perovskite/TiO$_2$ Interface

Landon Johnson, Dmitri Kilin, Aaron Forde, Yulun Han, Fatima B, Physics and Mathematics, North Dakota State University, Fargo, North Dakota, United States; Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota, United States; North Dakota State University, Fargo, North Dakota, United States.

Perovskite-based solar cells have been a popular research topic for the better part of the last decade due to their rapidly increasing power conversion efficiencies and ease of their fabrication. TiO$_2$ is frequently used as an electron transport material (ETM) in perovskite-based solar cells because of its low cost, low toxicity, versatility in sizes and structures, and chemical stability. Despite the successes of perovskites in solar cells, there are still aspects about their operation that are not fully understood. One example is the role of ligand groups acting as a bridge between the perovskite and ETM. This computational research aims to explore the effects that these ligand groups, which are adsorbed to a polycrystalline (TiO$_2$) for brevity) nanochaper, have on the photoexcited charge carrier dynamics within a perovskite-based solar cell. Density functional theory is used to find the ground state energies of the perovskite/TiO$_2$ solar cell as well as compute the molecular dynamics trajectory, where non-adiabatic electron-phonon couplings are calculated “on-the-fly.” These couplings are then used to calculate the Redfield tensor which is ultimately used to compute the photoexcited charge carrier dynamics. It is found that the ligand groups can alter the band gap, band alignment, charge transfer characteristics, accessible excitation pathways, and excited charge carrier lifetimes.

Resources


10:00 AM BREAK

10:30 AM ES15.11.06

Cirumventing Defects in Halide Perovskite Solar Cells Through the Application of Ferrocene Oxide Extraction Layers

Monica Lira-Cantu, Nanostructured Materials for Photovoltaic Energy Group, Catalan Institute of Nanoscience and Nanotechnology (ICN2), Bellaterra, Spain.

Highly stable halide perovskite solar cells employ semiconductor oxides as electron transport materials. Defects in these oxides, such as oxygen vacancies (O$_{vac}$), act as recombination centres and, under air and UV light, reduce the stability of the solar cell. Under the same conditions, the PbZrTiO$_3$ ferrocene oxide employs O$_{vac}$ for the creation of defect-dipoles responsible for photo-carrier separation and current transport, evading device degradation. We report the application of PbZrO$_3$ as the electron extraction material in triple cation halide perovskite solar cells. The application of a bias voltage (poling) up to 2 V, under UV light, is a critical step to induce charge transport in the ferrocene oxide. Champion cells result in power conversion efficiencies of ~11% after poling. Stability analysis, carried out at 1-sun AM 1.5 G, including UV light in air for unencapsulated devices, shows negligible degradation for hours in comparison with reference solar cells applying SnO$_2$ which degrades in only a few minutes. Our experiments indicate the effect of ferrocenyl from the PZT, however alternative conducting mechanisms affected by the accumulation of charges or the migration of ions (or the combination of them) can also be present. Our results demonstrate, for the first time, the application of ferrocene oxide as an electron extraction material in efficient and stable solar cells.
PSCs. These findings are also a step forward for the development of perovskite-based solar cells.


11:00 AM ES15.11.07

**Understanding the Energy Transfer Mechanism at the Perovskite—Organic Hybrid Interface**

Sarah Wieghold1, Juan-Pablo Correa-Baena2 and Lea Nienhaus1; 1Florida State University, Tallahassee, Florida, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

Understanding the energy transfer mechanism across hybrid interfaces which combine both inorganic and organic semiconductors is crucial in the advancement of optoelectronic devices. The exact energy transfer mechanism between inorganic and organic materials remains obscure, particularly where there is a large amount of structural inhomogeneity within the material.

Recent advances have shown that both lead sulfide (PbS) quantum dots, as well as CsPbX quantum dots are capable of efficient triplet energy transfer at such organic-inorganic hybrid interfaces.[1,2,3] Combining scanning probe microscopes with ensemble time-resolved optical spectroscopy, we investigate the underlying mechanism of energy transfer at hybrid interfaces comprised of lead halide perovskites and organic semiconductors. By understanding the interplay between the morphology and the band alignment arising from the perovskite composition, as well as the mechanism of the energy transfer at the hybrid interface, we can tailor our active materials to increase device performance by optimizing this energy transfer process.


11:15 AM ES15.11.08

**Ultra High Vacuum Scanning Probe Microscopy Investigations on Hybrid Organic Inorganic Perovskites**

Thibaut Gallet, Evandro Lanzoni, Christian Kameni Bounenou and Alex Redinger; University of Luxembourg, Esch/Alzette, Luxembourg.

Surface and interface passivation are of central importance for high efficiency perovskite solar devices. Despite the enormous efforts that have been undertaken in the last years to improve the power conversion efficiency of the devices, the surface properties are still not very well understood. Moreover, the polycrystallinity of the material leads to lateral fluctuations of the surface properties on the nanometer scale, which makes the analysis difficult and challenging. Scanning probe microscopy (SPM) techniques are ideal to gain a much deeper understanding of the surfaces and interfaces due to their high spatial resolution.

In this contribution, we present our results obtained on hybrid perovskites studied with scanning tunneling microscopy (STM) and spectroscopy (STS) combined with Kelvin Probe Force Microscopy (KPFM). All our studies have been carried out under ultra-high vacuum (UHV) conditions on clean absorbers that have not been exposed to air. In a first part, we show why ultra-high vacuum is indispensable for an accurate analysis of the nanometer scale properties. We compare KPFM measurements before and after air exposure in our UHV KPFM setup and compare the results to measurements under ambient conditions. In particular, we discuss the changes of the facet-dependent contrast of the grains, which is smeared out and reduced after air exposure, and we discuss the observed changes of the work function at the grain boundaries. Furthermore, we compare our results to the available literature.

In the second part, we discuss in detail the nanometer scale variations of coevaporated methylammonium lead iodide absorbers with minority carrier lifetimes exceeding one microsecond. In particular, we investigate the lateral variations of the workfunction on these absorbers layers and discuss the implications for the resulting solar cell devices. We will link our results from SPM to the specific growth conditions we used during synthesis.

Finally, we compare the results to another thin film technology, namely Cu(In,Ga)Se2. This comparison is essential to understand why hybrid organic inorganic perovskites outperform Cu(In,Ga)Se2 in terms of minority carrier lifetime and exceptionally high open-circuit voltages. In this part we use STS measurements to compare the local density of states of the perovskite and of the Cu(In,Ga)Se2 surfaces. It becomes evident from our measurements that the defect density at the surface is much lower for the perovskites, which underlines why these semiconductors perform so exceptionally well as well absorber layers in solar cells.

11:30 AM ES15.11.09

**Why Are Hot Holes Easier to Extract Than Hot Electrons From Halide Perovskite Solar Cells?**

Ibrahim Dursun, Partha Maiti, Jun Yin, Bekir Turedi, Ayan A. Zhumekenov, Kwang Joo Lee, Omar F. Mohammed and Osman Bakr; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The power conversion efficiency of light harvesting devices is limited by the rapid thermalization of charge carriers that are photoexcited with energies above the bandgap of the absorbing material. As these so-called ‘hot’ carriers are difficult to collect, their cooling places an upper bound on the available photon energy that a given solar cell may utilize. Recently, studies on hot carriers in methylammonium lead iodide (MAPbI3) perovskite have noted that they cooldown at an appreciably slower rate than carriers in other photovoltaic materials. However, the relaxation rate is still rapid in absolute terms, and hence, their capture and collection (before relaxing to the band edge) have not been shown so far. Here we demonstrate and explain the efficiency of hot carrier extraction from MAPbI3 using TiO2 and Spiro-OMeTAD as an electron transporting layer (ETL) and hole transporting layer (HTL), respectively, via real-time observation of the carrier dynamics with femtosecond transient absorption spectroscopy and supported by density functional theory (DFT) calculation. Time-resolved experiments have shown that a quasi-equilibrium distribution of hot carriers while not appreciably affected by the presence of TiO2 can be stabilized in a negative pressure environment with the application of hydrostatic tensile strain. Using density functional theory, we explore negative pressure induced phase transitions, and their consequent optoelectronic properties.

11:45 AM ES15.11.10

**Understanding the Nanocrystal Size Dependence of Phase Stability in CsPbI3**

Ruoxi Yang1, Aaron Fafarman2 and Liang Z. Tan1; 1Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States.

CsPbI3, a promising candidate for photovoltaic and light-emitting diode applications, is structurally unstable and transforms into an orthorhombic phase at room temperature. CsPbI3, in nanocrystal form, on the other hand, has displayed better thermal stability than in the bulk, and the stability depends on the size of the nanocrystal. Yet, not many studies have shed light on the underlying mechanisms. Using first-principles calculations, we demonstrate phase stability changes as a function of varying crystal size, which result from the competition between short-range bond formation and long-range electrostatic energies. Comparing these simulations with experiment, we show that this mechanism is analogous to the application of negative pressure, explaining the correlation between high-symmetry phase stability and nanostructuring. These results suggest that bulk phase CsPbI3 can be stabilized in a negative pressure environment with the application of hydrostatic tensile strain. Using density functional theory, we explore negative pressure induced phase transitions, and their consequent optoelectronic properties.
Halide Perovskites have a remarkably low defect density, especially if we consider the quick and “chimie douce” way of preparation of films as well as of most single crystals. The densities are all deduced from the common (all direct) measurements for charge or neutral defects. In this talk I will show how this behaviour reflects a quite fundamental property of these materials, with a rather simple basis. The talk will combine experimental results from several sources, including our own, for thermodynamic, optical, and electrical data. It is plausible that our conclusions can be generalized to help look for other ultra-low defect density materials.

Thanks to David Egger (Regensburg), Omer Yaffe and Leocor Kronik (Weizmann Inst.)

2:00 PM *ES15.12.02
Following Free Carrier Formation and the Generation of Coherent Optical Phonons in Lead Iodide Perovskite Sanford Ruhman

Under solar irradiation, most photons absorbed in methyl ammonium lead iodide perovskite (MAPbI$_3$) possess ~0.4 eV of excess energy above the 1.65 eV band gap (BG), and characterizing the important stages of free carrier generation and relaxation dynamics requires ultrafast spectroscopic investigation. Carrier cooling and recombination in hybrid perovskites occurs in ps and ns timescales respectively. Probing exciton dissociation however requires extreme (sub-10 fs) time resolution. The significance of optical phonon coupling to free carriers in these materials (polarons) has recently been the subject of lively debate. To date only a few time domain measurements have reported impulsive phonon activity, and those reports have not converged in terms of the active phonon frequencies or coupling strengths. Here, we present high S/N sub-10 fs pump-probe spectroscopy of MAPbI$_3$ films to record ultrafast exciton dissociation, which has not been reported previously. High above band gap excitation in MAPbI$_3$ provides an opportunity to observe free carrier generation followed by cooling dynamics. Transient transmission (TT) spectra of MAPbI$_3$ films after photoexcitation reveal a number of features which are common to previous pump-probe studies of this system. First, a photoinduced bleach at the optical BG which appears constantly and grows to its full magnitude during carrier cooling, is attributed to hot carrier induced screening of the exciton transition and state filling. Another is an absorption feature rising below the band edge assigned to band gap renormalization and shifting of exciton transition. This feature also appears immediately after excitation, but decays over the carrier cooling stage. The third is a slow rising broad induced absorption feature in the inter-band region. Using the extreme time resolution here, a sharp red shift of exciton transition is observed at early times. Surprisingly, the photoinduced band bleach derived by extracting a band integral over the whole probing range, appears abruptly with a delay of 20 fs after the pump excitation. This delay in rising of band integral bleach is assigned to exciton dissociation or the breakup of localized e-h pair. To the best of our knowledge this is the first recording of this phase of free carrier formation following above BG photoexcitation in this material, or in bulk semiconductors. Observing this phase hinges on the ultrashort pump pulses ability to generate such localized carrier pairs even high above the BG due to coherent excitation of a broad band of “k” states. Finally, the delayed ~0.4 ps rise of the band integral is compatible with carrier cooling.

The pump-probe spectra also reveal weak periodic modulations. The residual modulations at different probe wavelengths were extracted by subtracting the transient signal. The Fourier analysis of the residual modulation detects predominantly two of active phonon modes: low frequency mode ~110 cm$^{-1}$ and a high frequency mode ~240 cm$^{-1}$ assigned to the torsions of methylammonium cation (Fig. 2d). The amplitudes of these spectral modulations were used to estimate the electron-phonon coupling strength, assuming a displaced harmonic oscillator model. The estimated coupling strengths (Huang-Rhys parameter, S: 0.02-0.04) for the MAPbI$_3$ films are well within the weak coupling regime, which is compatible with free carriers existing as large polarons in these materials. These observed phonon modes may not be responsible for perovskite’s moderate carrier mobility, which requires intermediate electron-phonon coupling.

In conclusion, sub 10fs above band gap pump-probe data resuggest that, instantly generated localized hot excitons dissociate to free carriers within ~20 fs. Faint spectral modulations in the transient signals are assigned to coherent phonons. These modulations are assigned to longitudinal optical (LO) phonons weakly coupled to the electronic transition.

3:00 PM *ES15.12.03
Phonon Coherences Reveal the Polaronic Character of Excitons in Two-Dimensional Lead Halide Perovskites Felix Thouin, David A. Valverde Chavez, Ilaria Bargigia, Daniele Cortecchia, Annamaria Petrozza, David Beljonne, Ajay R. Srimath Kandada and Carlo Silva; Georgia Institute of Technology, Atlanta, Georgia, United States; 2Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, Milan, Italy; 3Laboratory for Chemistry of Novel Materials, Université de Mons, Mons, Belgium.

Hybrid organic-inorganic semiconductors feature complex lattice dynamics due to the “softness” arising from non-covalent bonds between molecular moieties and the inorganic network, and to the ionic character of the crystal. Such complex lattice motion has profound consequences on the fundamental character of primary photoexcitations with respect to purely covalent semiconductor crystals. In this work, we establish that this dynamic structural complexity gives rise to the coexistence of diverse excitonic resonances in a prototypical two-dimensional lead iodide perovskite, each with a distinct degree of polaronic character. By means of high-resolution resonant impulsive stimulated Raman spectroscopy, we address the coupling of both charge carriers and excitons to low-frequency optical phonons (those with frequency ≤ 50 cm$^{-1}$). Resonant photoexcitation results in vibrational wavepacket dynamics that evolve along different configurational coordinates for distinct excitons and photocarriers. Employing density functional theory calculations, we assign the observed coherent vibrational modes to various phonons involving motion in the lead-iodide layers. We thus conclude that different excitons induce specific lattice reorganizations that are distinct from those involving charge carriers, which are signatures of polaronic binding. Our conclusions provide a novel perspective of the energetic/configurational landscape involving globally neutral primary photoexcitations in a broad class of emerging hybrid semiconductor materials.

3:30 PM *ES15.12.04
Evidence of Electronically Decoupled Organic and Inorganic Sublattices in Methylammonium Lead Iodide from Infrared Vibrational Excitation Peijun Guo, Arun Kumar Mannodi Kanakkithodi, Jue Gong, Yi Xia, Tao Xu, Maria K. Chan, Mercouri G. Kanatzidis and Richard D. Schaller; 1Argonne National Laboratory, Lemont, Illinois, United States; 2Northwestern University, Evanston, Illinois, United States; 3Northwestern University, Evanston, Illinois, United States.

Organic-inorganic hybrid perovskites such as methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) are solution-processable semiconductors for high-efficiency solar cells and light-emitting devices owing to their long carrier lifetime and diffusion length. Determining whether the solar organic cations with strong dynamic disorder benefit the optoelectronic properties of CH$_3$NH$_3$PbI$_3$ has been challenging. Herein, via transient absorption measurements employing an infrared pump tuned to a methylammonium N-H stretching vibration, we observe vibrational energy transfer from the selectively excited organic mode to the entire crystal lattice in nanosecond timescale. The observed transient electronic signatures, during the period of thermal-nonequilibrium when the induced thermal motions are mostly concentrated on the organic sublattice, reveal that the induced motions of the organic cations do not apparently alter absorption or photoluminescence response of CH$_3$NH$_3$PbI$_3$, beyond thermal effects. Our results suggest that the attractive optoelectronic properties of CH$_3$NH$_3$PbI$_3$ mainly derive from the inorganic lead-halide framework.

3:45 PM *ES15.12.05
Light Emitting Diodes Based on Inorganic Composite Halide Perovskites Xiujuan Lian, Xi Wang and Hanwei Gao; Physics, Florida State University, Tallahassee, Florida, United States.
CsPbBr₃ is a promising type of light-emitting halide perovskite with inorganic composition and desirable thermal stability. The luminescence efficiency of pristine CsPbBr₃ thin films, however, appears to be limited. In this work, light emitting diodes based on CsPbBr₃:CsPbBr₆ composites are demonstrated. Both quantum efficiency and emission brightness are improved significantly compared with similar devices constructed using pure CsPbBr₃. The high brightness can be attributed to the enhanced radiative recombination from CsPbBr₆ crystallites confined in the CsPbBr₃ host matrix. The unfavorable charge transport property of CsPbBr₆ can be circumvented by optimizing the ratio between the host and the guest components and the total thickness of the composite thin films. The inorganic composition of the emitting layer also leads to improved device stability under the condition of continuous operation.

4:00 PM ES15.12.06
Coherent Spin and Quasi-Particle Dynamics in Two-Dimensional Lead Halide Perovskites David Giovannii², Herlina A. Dewi², ³, Subodhi Mhaisalkar², ³, Neeraj Mathews¹ and Tze Chien Sun¹; ¹School of Material Science and Engineering, Nanyang Technological University, Singapore, Singapore; ²School of Physical and Mathematical Sciences, Department of Physics and Applied Physics, Nanyang Technological University, Singapore, Singapore; ³Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore.

Layered 2D halide perovskites, with their alternating organic and inorganic atomic layers that form self-assembled multi-quantum wells (MQW), have been shown to possess robust light-matter coupling, owing to quantum and dielectric confinement effect. Within their periodic structures lie a hotbed of robust photophysical phenomena, rising from the coherent quantum-mechanical interplays between exciton, spin, phonon, and photon. Herein, we explicate these intricate dynamics via transient absorption spectroscopy. Few to be highlighted here are: (i) the robust spin-selective optical Stark effect, which are few times stronger than in conventional inorganic semiconductors; (ii) ultrafast carrier thermalization and spin relaxation via exchange interaction; and (iii) strong coherent exciton-photon coupling. Origin of transient spectral features and exciton relaxation pathways are also revealed from detailed phenomenological modelling of the transient dynamics. Importantly, our work unravels the understanding of complex optical spin and quasi-particle interactions in these layered 2D halide perovskites, which are the key to exploit their full potential.

4:15 PM ES15.12.07
Structural Dynamics in Hybrid Halide Perovskites—Bulk Rashba Splitting and Carrier Localization Chao Zheng¹, Shidong Yu¹, ² and Oleg Rubel¹; ¹Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; ²College of Materials Science and Engineering, Jilin University, Changchun City, China.

The extended carrier lifetime in hybrid halide perovskites was attributed to a quasi-indirect band gap that arises due to Rashba splitting in both conduction and valence band edges. We will present results for an effective relativistic band structure of (CH₃NH₃)₂PbI₆ with focus on the dispersion of electronic states near the band edges of (CH₃NH₃)₂PbI₆ affected by thermal structural fluctuations [1]. We establish a relation between the magnitude of Rashba splitting and the deviation of Pb-atom from its center-symmetric site in the PbOoctahedron. In order for the splitting energy to reach the thermal energy of 26 meV (room temperature), the displacement should be of the order 0.3 Ang, which is far above the static displacements of 0.1 Ang for Pb-atoms in the tetragonal phase of (CH₃NH₃)₂PbI₆.

The significant dynamic enhancement of the Rashba splitting observed at earlier simulation times (less than 2 ps) later weakens and becomes less than the thermal energy despite the average displacement of Pb-atoms remaining large (0.37 Ang). It is randomization of Pb-displacement vectors and associated cancelation of the net effective magnetic field acting on electrons at the conduction band edge is responsible for reduction of the Rashba splitting.

The lattice dynamics also leads to deterioration of Bloch character [2] for states in the valence band, which leads to charge localization in (CH₃NH₃)₂PbI₆, is therefore affected. These results call into question the quasi-indirect band gap as a reason for the long carrier lifetime observed in (CH₃NH₃)₂PbI₆ at room temperature. An alternative mechanism involves dynamic localization of holes and their reduced overlap with electrons in reciprocal space.


4:30 PM ES15.12.08
Nonlinear Optical Responses of MAPbCl₃ Perovskite Single Crystals Studied by Z-Scan Method Keiichi Ohara, Hirokazu Tahara, Takumi Yamada, Tomoko Aharen, Hideki Hiori and Yoshishiko Kanemitsu; Kyoto University, Uji, Japan.

In recent years, there have been extensive studies made on optical and electronic properties of lead halide perovskite semiconductors, MAPbX₃ (MA = CH₃NH₃, X = I, Br, and Cl) from the fundamental physics viewpoint and from the interest in the application to functional photonic devices [1]. These direct-gap semiconductors exhibit sharp absorption spectra with very small Urbach energies, strong light emission with no essential Stokes shift, and long carrier diffusion lengths, leading to high energy conversion efficiencies of solar cells. Besides solar cell applications, MAPbX₃ perovskites are considered as materials for light-emitting diodes, lasers, optical modulators, and nonlinear optical crystals [2-4]. Especially, it is very important to elucidate their nonlinear optical response for future device applications. Among them, a wide-gap semiconductor MAPbI₃ has attracted attention as a photonic device material in the blue spectral region [2].

In this work, we clarify the nonlinear refractive index and nonlinear absorption coefficient of MAPbCl₃ single crystals and their wavelength dependence. The thin film sample of MAPbCl₃ has a grain structure and strong light scattering occurs in the blue spectral region, being an obstacle for measuring their essential optical characteristics. In order to eliminate the influence of light scattering, a large bulk single crystal was used. Third-order nonlinear optical coefficients were determined by the Z-scan method. We determined the nonlinear refractive index from the close aperture measurement and the nonlinear absorption coefficient from the open aperture measurement at various excitation wavelengths. Nonlinear optical responses can be explained by a simple two band model. Our measurements clearly shows that MAPbCl₃ perovskites are simple direct-gap semiconductors and the nonlinear optical coefficients are comparable to GaAs single crystals [5].

Part of this work was supported by JST-CREST (JPMJCR16N3).


4:45 PM ES15.12.09
Efficient Anti-Stokes Photoluminescence from CH₃NH₃PbI₃ Perovskite Semiconductors Takumi Yamada, Tomoko Aharen and Yoshishiko Kanemitsu; Kyoto University, Kyoto, Japan.

Organic-inorganic hybrid perovskite semiconductors are collecting much attention as a new class of optical device materials. In particular, CH₃NH₃PbI₃ (MAPbI₃) shows highly efficient photoluminescence (PL) with no Stokes shift even at room temperature due to the band-to-band transition. Many unique optical phenomena based on efficient PL with no Stokes shift, such as photon recycling and radiative cooling, have been discussed [1,2]. Photon recycling is caused by the repeated light emission and reabsorption processes. The laser cooling of semiconductors is induced by anti-Stokes PL (AS-PL) via photon absorption. One important factor to anti-Stokes phenomena in semiconductors is a high external quantum efficiency (EQE). However, laser cooling has not been achieved even for GaAs/GaInP quantum well with EQE of 99.5% [3]. Therefore, it is important to clarify the material properties and experimental conditions required for laser cooling. Specifically, it is necessary to clarify the physics of AS-PL and its reabsorption in the perovskites by employing both optically thin and thick samples.

In this study, we prepared optically thin film and thick single crystal of MAPbI₃, and investigated their AS-PL characteristics [4]. Using PL excitation (PLE) spectroscopy, we determined the excitation-energy dependence of the AS-PL and the Stokes PL (S-PL) by dividing the PL spectrum into anti-Stokes and Stokes parts. We obtained the up-conversion gain spectrum defined as the intensity difference between the AS-PLE and S-PLE spectra. The gain spectra showed a broad spectral shape and its maximum point was located below the balanced point where the anti-Stokes PLE and Stokes PLE intensities become equal. The broad shape of the up-conversion gain spectrum suggests that unique phonon dynamics, such as large anharmonicity and polaron formation, play an important role of efficient up-conversion process in the perovskites.

Part of this work was supported by JST-CREST (JPMJCR16N3) and JSPS Research Fellowships for Young Scientists (17J08790).

In Situ 8:15 AM
doing this, i.e. by exciting a single photon up-conversion
phenomenon has recently been demonstrated in CsPbBr nanocrystals with an external quantum efficiency greater than 70%. This high efficiency seems to odd with previous studies, as perovskite nanocrystals are known to generally lack mid-gap states.

This presentation will discuss our recent progress in examining one photon up-conversion in all-inorganic perovskite nanocrystals, especially regarding the potential role of an intermediate state in the excitation process, as well as the optimization of the up-conversion via plasmonic enhancement in systems coupled to metal nanoparticles. Specifically, we have shown that a facile surface treatment increases the efficiency of one photon up-conversion in CsPbBr nanocrystals, even if it increases the traditional down-converted photoluminescence quantum yield to essentially unity indicating a lack of mid-gap trap states. This increase in up-conversion efficiency, despite the lack of mid-gap states, suggests that such states act as loss pathways rather than acting as intermediate states necessary to the excitation mechanism. Additionally, we show that through the presence of a localized surface plasmon, e.g. by depositing gold nanoparticles, the observed up-conversion blue shifts, indicating more efficient use of thermal energy to drive optical emission. These results suggest another mechanism may be the key to understanding and optimizing one photon up-conversion, one that does not involve discrete mid-gap states. The efficiency of this up-conversion mechanism in CsPbBr makes this material a good candidate for optically driven cooling. As such, we will also discuss initial thermometry studies of cooling power in perovskite nanocrystal films.

8:15 AM ES15.13.02
In Situ Transient Absorption Spectroscopy of Perovskite Nanocrystal Formation and Growth

Methyllammonium lead halide perovskites have attracted significant interest for their desirable electronic properties. Nanocrystals formed from these materials have shown great promise for use in LEDs and lasers due to their high fluorescence quantum yield and the tunability of their emission throughout the visible spectrum. The rapid kinetics of common nanocrystal syntheses such as hot-injection – combined with the inherent instability of the partially capped nucleation centers that are nascent nanocrystals – precludes the use of time-resolved spectroscopy to measure the evolution of excited state dynamics during the formation of fully passivated nanocrystals. The ability to measure electronic structure and dynamics during this process would deepen our understanding of the relationship between synthetic parameters and the resulting functional electronic properties. Here we use an ambient, room temperature ligand-mediated nanocrystal synthesis with reaction timescales more favorable for study via transient absorption (TA) spectroscopy. By coupling this synthesis with transient absorption spectroscopy, we are able to provide the first ever characterization of excited state dynamics in unstable, immature perovskite nanocrystals as they grow and their surfaces are capped with passivating ligands. We observe a previously unreported signature in the TA spectrum of immature nanocrystals that is not present in fully formed nanocrystals. This work helps elucidate the role the surface of these materials plays in excited state dynamics, as well as providing new insight into the evolution of exciton dynamics during perovskite nanocrystal growth and formation. Future measurements utilizing a single-shot transient absorption (ssTA) spectrometer that is capable of measuring entire transients in a few seconds will enable the spectroscopic observation of nanocrystal syntheses in real-time.

8:30 AM ES15.13.03
Bright Triplet Excitons in Cesium Lead Halide Perovskites

The observation of a ground optically forbidden “dark” exciton state in semiconductor nanocrystals was first reported in the seminal paper of Nirmal et al. in 1995. Later research in nanowires, nanorods, and nanodot systems has shown that the ground exciton state in all these semiconductor structures is a dark exciton, leading us to believe that the ground exciton must be dark. Because dark excitons release photons slowly, hindering emission, semiconductor nanostructures that disobey this rule have been sought. However, despite considerable experimental and theoretical efforts, no nanocrystals have been identified in which the lowest exciton is bright. Three years ago however cesium lead halide perovskite (CsPbX3, with X = Cl, Br or I) nanocrystals were grown, which without too much effort, demonstrated very bright photoluminescence (PL) with quantum yield 50-90% at room temperature. This bright emission was traced to a very short radiative decay time. The nanocrystals emit light about 20 and 1,000 times faster than any other semiconductor nanocrystal at room and cryogenic temperatures, respectively. The increase of the decay time with temperature is inconsistent with a dark ground state exciton, suggesting that in these nanocrystals the ground exciton state is bright. We use an effective-mass model and group theory to demonstrate the possibility of such a ground bright exciton must be dark. Because dark excitons release photons slowly, hindering emission, semiconductor nanostructures that disobey this rule have been sought. However, despite considerable experimental and theoretical efforts, no nanocrystals have been identified in which the lowest exciton is bright. Three years ago however cesium lead halide perovskite (CsPbX3, with X = Cl, Br or I) nanocrystals were grown, which without too much effort, demonstrated very bright photoluminescence (PL) with quantum yield 50-90% at room temperature. This bright emission was traced to a very short radiative decay time. The nanocrystals emit light about 20 and 1,000 times faster than any other semiconductor nanocrystal at room and cryogenic temperatures, respectively. The increase of the decay time with temperature is inconsistent with a dark ground state exciton, suggesting that in these nanocrystals the ground exciton state is bright. We use an effective-mass model and group theory to demonstrate the possibility of such a ground bright exciton.
such more device-oriented structures give further insight into the complete charge separation process as it occurs in corresponding photodetectors.

SESSION ES15.14: Emissive Behaviour and Defects Physics
Session Chairs: Alexander Efros and Carlos Silva
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 130

9:15 AM *ES15.14.01
Strong Exciton–Photon Coupling in Perovskite Microcavities Xin Feng Liu; NCNST, Beijing, China.

Hybrid organic-inorganic perovskites (HOIPs) are low-cost and highly efficient optoelectronic and photovoltaic materials for applications in solar cells, emitting diodes (LEDs)[1-3], and so on, which is correlated with their intrinsic structures. Now the hybrid perovskite families include three-dimensional (3D) (CH$_3$NH$_3$PbX$_3$), two-dimensional (2D) ((C$_6$H$_5$NH$_3$)$_2$PbI$_3$) and nanostructured (CH$_3$NH$_3$PbBr$_3$ nanoparticles) materials. However, physical exploration to such materials is still at early stage and full assessment of their structures and properties is still missing.

High pressure[4] and various temperature[5] allow easy access to various structures and interactions among the constituent atoms and molecules, which will in return significantly change the corresponding physical and chemical properties. Therefore, exploring correlations between pressure-induced structural and electronic changes of hybrid perovskites is essential to well understand the intrinsic structural stability and establish structure-property relationship for optimizing their functionality in practical long-term applications.

Importantly, up to now, realizing the controlled growth of two dimensional perovskite at sub-10 nm scale remains a great challenge, which has largely limited the development and applications of two dimensional perovskites. We employed the atomic crystal modulated photoluminescence imaging and obtained the carrier mobility of about 28 cm$^2$/Vs. Meanwhile, we achieved high quality laser arrays based on the in-plane directional CsPbX$_2$ materials, which also show composition-dependent strong exciton-photon coupling[6]. Unfortunately, the devices based on perovskite nanostructures still need improvement due to their environmental instability and device fabrication process incompatibility. To address these problems, we report a novel laser devices fabricated by directly growing CsPbBr$_3$ nanoparticles on prepatterned indium tin oxide (ITO) electrodes via a vapor-phase deposition[7]. Besides, we demonstrate the visualizing carrier transport of these all-inorganic CsPbBr$_3$ perovskite nanoparticles by electric field modulated photoluminescence imaging and obtained the carrier mobility of about 28 cm$^2$/Vs[8]. Importantly, up to now, realizing the controlled growth of two dimensional perovskite at sub-10 nm scale remains a great challenge, which has largely limited the development and applications of two dimensional perovskites. We employed the atomic crystal semiconductor such as TMDs (eg. WS$_2$, MoS$_2$) as substrate materials, and obtained uniform TMDs/Perovskite hybrid heterostructures, with the thickness can be well controlled at sub-10 nm scale. These results suggest that the novel low dimensional perovskite nanostructures may open up new opportunities for various applications in integrated electronics, optoelectronics, and quantum electronics.

References:

10:00 AM BREAK

10:30 AM *ES15.14.03
Controlled Synthesis and Photonics Applications of Low Dimensional Metal Halide Perovskites Anlian Pan; College of Materials Science and Engineering, Hunan University, Changsha, China.

Low dimensional halide perovskites have attracted enormous attention due to their superior optical and electronic properties. Very recently, intense research has been directed toward the fabrication of the low dimension perovskite materials for laser applications, the performance of such lasers is highly dependent on the quality of the material and cavity, which makes it challenging. Herein, we demonstrate that cesium lead halide perovskite nanorods fabricated via vapor methods, which can also serve as gain media and effective cavities for tunable lasers[9]. Meanwhile, we have also achieved single-mode laser based on cesium lead halide perovskite submicron sphere at room temperature[10]. Furthermore, we achieved epitaxial growth of single-crystal cesium lead bromide perovskite film on Metal Oxide Perovskite (SrTiO$_3$) and developed a novel vapor-solution method for preparation of high-quality perovskite films on flexible substrates[11], both perovskite based structures show high-performance in photodetection among visible light. Moreover, the photodetector can be extended to near-infrared range through designing novel perovskite–erbium silicate nanosheet hybrid structures, which exhibit remarkable spectral response at ~1.54 μm[12]. Considering the perovskite based application, we demonstrated the controlled growth of in-plane directional perovskite CsPbBr$_3$ nanowires on annealed M-plane sapphire substrates, and the guided nanowire exhibit excellent photoresponse properties a very fast response speed[13]. In addition, we achieved high quality laser arrays based on the in-plane directional CsPbX$_2$ perovskite nanowires, which also show composition-dependent strong exciton-photon coupling[14]. Unfortunately, the devices based on perovskite nanostructures still need improvement due to their environmental instability and device fabrication process incompatibility. To address these problems, we report a novel laser devices fabricated by directly growing CsPbBr$_3$ nanoparticles on prepatterned indium tin oxide (ITO) electrodes via a vapor-phase deposition[15]. Besides, we demonstrate the visualizing carrier transport of these all-inorganic CsPbBr$_3$ perovskite nanoparticles by electric field modulated photoluminescence imaging and obtained the carrier mobility of about 28 cm$^2$/Vs[16]. Importantly, up to now, realizing the controlled growth of two dimensional perovskite at sub-10 nm scale remains a great challenge, which has largely limited the development and applications of two dimensional perovskites. We employed the atomic crystal semiconductor such as TMDs (eg. WS$_2$, MoS$_2$) as substrate materials, and obtained uniform TMDs/Perovskite hybrid heterostructures, with the thickness can be well controlled at sub-10 nm scale. These results suggest that the novel low dimension perovskite nanostructures may open up new opportunities for various applications in integrated electronics, optoelectronics, and quantum electronics.

References:

11:00 AM ES15.14.04
Dynamics and Interfacial Effects of Intrinsic Surface Defects at the Atomic-Scale in CH$_3$NH$_3$PbBr$_3$ Collin Stecker$^1$, Kesi Liu$^2$, Jeremy Hieule$^1$, Zhenyu Liu$^2$, Robin Ohmann$^1$, Luis K. Ono$^1$, Guofeng Wang$^1$; ‘Okinawa Institute of Science and Technology, Okinawa, Japan; ‘Swanson School of Engineering, University of
Understanding the nature of defects in organic-inorganic hybrid perovskites (OHPs) is one of the key challenges to improving perovskite-based devices. Surface defects are of special interest because they exist at interfaces in the final device. The concept of ion migration has been used to explain the anomalous current-voltage hysteresis phenomenon observed in hybrid organic-inorganic perovskites (OHPs), and has also been implicated as potential cause for long-term material degradation. Theoretical studies have predicted vacancy assisted migration may be a possible mechanism, but the dynamics that occur at the atomic scale are still not well clarified experimentally. Scanning tunneling microscopy (STM) offers the ability to probe the surface of OHPs with atomic resolution, including resolving individual vacancy defects. Scanning the same area multiple times allows for observation of dynamic events. Here, ion migration to and from the surface was imaged at the atomic scale, and DFT calculations indicate that a step-wise mechanism for migration of MABr vacancies is energetically favorable, shedding light on the mechanism by which vacancy-assisted ion migration occurs. It is also shown that the presence of surface vacancies affects the local work function, which has implications for charge transfer between layers in a device.

References
Various modulation spectroscopic methods have been developed and employed in the PV research; impedance, capacitance, admittance, light-intensity modulation, to name a few. Each of them is built on its own physical picture, whose basic notion has long been tested and the validity confirmed, at least in the inorganic semiconductor research. However, once these techniques are applied to the perovskite PVS, we have encountered difficulties in interpreting the data in a consistent manner. It is now clear that the culprit is the ion motion, which is as influential as electron motion in some cases. We will try to reinterpret the conflicting results from the point of view of the ion motion.

In the modulation spectroscopy, one usually modulates the applied potential or the carrier density. The response would be the extracted current or the voltage across the device. As the word “spectroscopy” implies, one measures the response as a function of the modulation frequency in the linear regime, i.e., with the small enough modulation depth so that nonlinearity does not enter. The out-of-phase response normally carries the important information because it reflects the carrier dynamics in the device. In the traditional inorganic PVS, only electrons are the charge carriers. Despite this simplicity, it is hard to distinguish various mechanisms, notable examples being (1) charge trapping-detrapping processes and (2) Maxwell-Wagner polarization. The response becomes multiplicatively more complex in the presence of ions, because the (3) ionic motion not only causes displacement current but also changes the internal electrostatic potential landscape affecting the electron distribution. The three processes enumerated above all fall in similar frequency ranges** so that it is hard to distinguish them.

We have performed various modulation spectroscopy experiments and numerical simulations. Model calculations of the three processes above reveal the signatures one should look for in the data peculiar to each process. Therefore, it is of essential importance to analyze the same set of data in detail and in various ways. We will review our effort in analyzing the data to identify the processes inside the perovskite PVS. The responses as a function of frequency, temperature, illumination intensity and wavelength are combined to arrive at an overall semi-quantitative picture. We will present exemplifying results.

* Although this aspect is not often discussed in the literature, one needs to pay attention to what extent a particular experiment perturbs the system. It is important when data from different types of modulation experiments are compared.

** It is not clear if this is accidental or if there is underlying physics, i.e., correlated ion-electron motion mediated by defects.

1:20 PM ES15.15.02
Imaging Ion Distribution in Mixed-Halide Lead Perovskites Sarah Wieghold1, Juan-Pablo Correa-Baena2 and Lea Nienhaus1; 3Florida State University, Tallahassee, Florida, United States; 2Georgia Institute of Technology, Atlanta, Georgia, United States.

A key debate involving mixed-cation lead-mixed-halide perovskite thin films relates to the effects of process conditions on film morphology and local performance of perovskite solar cells. The halide distribution in these thin films has been shown to be of great importance for optoelectronic properties and device performances [1]. In particular, in mixed Br/I perovskites with high Br content, the thin films exhibit multiple emission peaks, suggesting segregation of halides [2]. To understand the underlying mechanisms, we map the spatial distribution of the ions in these complex multi-element halide lead perovskite thin films by synchrotron-based nanoprobe X-ray fluorescence (n-XRF). To get more insights into the growth mechanism and the resulting distribution of the halides and alkali ions, we fabricate films with different thicknesses and use scanning probe techniques as well as time-resolved optical spectroscopy. These insights into the interplay between composition, microstructure, and macroscopic properties pave the way to improved performance in this rapidly growing family of multinary lead-halide materials for solar cell applications.


1:25 PM ES15.15.03
Ion Migration in Hybrid Perovskite and the Consequences for Solar Cells Lucie McGovern, Moritz H. Futscher and Bruno Ehler; FOM Institute AMOLF, Amsterdam, Netherlands.

Solar cells based on organic-inorganic halide perovskites have entered the research field of photovoltaics by storm, already reaching efficiencies close to highly optimized silicon solar cells. In this context ion migration has been drastically influenced perovskites properties at various timescales. To understand the effect of ion migration we compare differently prepared perovskite devices, where we determine activation energies, concentrations and diffusion coefficients of mobile ions using transient ion drift and admittance spectroscopy. We show a correlation between fabrication conditions and ion migration. Our results shed light on the strong influence on the exact fabrication conditions, and will help to develop more robust protocols for the fabrication of highly efficient perovskite devices.

2:30 PM ES15.15.04
Halide Diffusion and Phase Stability in Mixed-Halide Perovskite-Perovskite Lateral Heterostructures Rhiannon (Rhys) M. Kennard1, Clayton J. Dahlman1, Hidenori Nakayama2, Kunal Mukherjee3, Ram Seshadri1 and Michael L. Chabinyc1; 1University of California, Santa Barbara, Santa Barbara, California, United States; 2Mitsubishi Chemical Corporation, Yokohama, Japan.

Mixed-halide perovskites are strong candidates for tandem solar cells and light-emitting devices because they exhibit bandgap tunability over the entire visible spectrum, which is easily accomplished via halide mixing. The most efficient solar cells employ a mixture of halides (typically bromide and iodide) and cations to stabilize the perovskite phase while easily accomplished via halide mixing. The most efficient solar cells employ a mixture of halides (typically bromide and iodide) and cations to stabilize the perovskite phase while effectively controlling the bandgap. The Br/I perovskites with high Br content, the thin films exhibit multiple emission peaks, suggesting segregation of halides [2]. To understand the underlying mechanisms, we map the spatial distribution of the ions in these complex multi-element halide lead perovskite thin films by synchrotron-based nanoprobe X-ray fluorescence (n-XRF). To get more insights into the growth mechanism and the resulting distribution of the halides and alkali ions, we fabricate films with different thicknesses and use scanning probe techniques as well as time-resolved optical spectroscopy. These insights into the interplay between composition, microstructure, and macroscopic properties pave the way to improved performance in this rapidly growing family of multinary lead-halide materials for solar cell applications.


2:45 PM ES15.15.05
Ion Migration in Mixed-Halide Perovskite Nanostructures Xiaoyong Wang1, Huichao Zhang1, Xu Fu1, Ying Tang2, William Yu3 and Min Xiao1, 2; 1Nanjing University, Nanjing, China; 2Jilin University, Changchun, China; 3University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States.

Semiconductor perovskites of methylammonium (MA) lead halide (MAPbX3, X = Br, Cl, I or mixtures thereof) have been drawing great research attention due to their superior performance in solar cells with a rapidly-rising photo-conversion efficiency towards that of the crystalline silicon counterparts. The main obstacle for commercial advancement of these organolead halide solar cells lies in the instability and degradation of light-harvesting MAPbX3 films. Especially bothersome is the ion migration effect, which is believed to be responsible for the slow conductivity response, anomalous current-voltage hysteresis, giant dielectric constant and switchable photocurrent in the MAPbI3 perovskites. Meanwhile, ion migration is manifested in mixed-halide MAPbBrI1x (0 < x < 3) perovskites as a light-induced segregation of iodide- and bromide-rich domains that can revert
back to the original phase in the dark. The iodide-rich domains in the MAPbBr$_{3-x}$ perovskites would cause a red shift in the photoluminescence (PL) that has been similarly observed in the CsPbBr$_{3-x}$ perovskites, confirming a universal role played by the migration of halide ions in the light-induced phase separation process. In addition to the bulk mixed-halide perovskites mentioned above, the phase separation effect has also been observed in the CsPbBr$_{3-x}$ nanocrystals (NCs) albeit from the photoluminescence measurements. Given the nanoscale size of the iodide-rich domain that are preferentially located along the grain boundaries of the bulk mixed-halide perovskites, the CsPbBr$_{3-x}$ NCs with a normally defective surface could provide a succinct understanding of the phase separation process from a bottom-up point of view.

Here we focus on mixed-halide CsPbBr$_{3-x}$ NCs to investigate the phase separation effect at both the ensemble-film and the single-particle levels. With laser excitation, the ensemble film of CsPbBr$_{3-x}$ NCs demonstrates a blue shift from ~630 to ~520 nm in the PL that can revert back in the dark, which can be attributed to the migration of iodide ions out of and back to the excitation volume. For an isolated single CsPbBr$_{3-x}$ NC, the PL is also blue shifted upon laser excitation but never returns back in the dark, signifying the necessary existence of nearby NCs to channel the migration of iodide ions. Interestingly, the blue-shifted PL can also be induced when the CsPbBr$_{3-x}$ NCs are electrically biased in the dark without the injection of excited-state charge carriers. This strongly suggests that it is the local electric field to break the iodide bonds that triggers the ion migration process in photo-excited CsPbBr$_{3-x}$ NCs. While the enlarged energy bandgap is mainly caused by bromide enrichment in the mixed-halide CsPbBr$_{3-x}$ NCs, we additionally show that lattice distortion by the migration of iodide ions could also make a minor contribution, as verified by the observation of a blue shift in the PL as large as 20 nm from the single-halide CsPbI$_x$ NCs upon laser excitation.

Except the blue-shifted PL, we believe that the ion migration mechanism proposed above could also be employed to describe the phase segregation processes observed in all the other mixed-halide perovskite materials. A spatial size of tens of nanometers are normally required for the formation of a iodide-rich domain in bulk films of the mixed-halide perovskites, which is obviously difficult to be accommodated in any single CsPbBr$_{3-x}$ NC to trap the photo-excitcated excitons, so that they would recombine with a photon energy dictated by the bandgap of the bromide-rich domains.

3:00 PM BREAK

SESSION ES15.16: Novel Photophysics and Quasi-Particle Phenomena II
Session Chairs: Kenjiro Miyano and Yabing Qi
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 130

3:30 PM *ES15.16.01
Small and Large Polarons in 2D and 3D Hybrid Perovskites


Due to the highly deformable and polar nature of the metal halide framework, hybrid perovskites are very prone to lattice relaxation, which causes self-trapping of the elementary excitations into phonon-dressed localized states. In low-dimensional perovskites (e.g. 2D structures), where Coulomb interactions are enhanced by reduced dielectric screening and quantum confinement effects, the formation of self-trapped excitons (small polarons) manifests itself in apparent radiative recombination effects. Ab-initio calculations have indicated that the excess charge is spatially confined to one crystal unit cell or less, inducing local distortions of the inorganic layers. Photoexcitation in 2D perovskites gives rise to photoinduced lattice deformations associated to polaronic exciton states, with a characteristic fine structure in the absorption line-shapes. On the other hand, for charge carriers in 3D perovskites, the lattice distortion leads to the formation of charged polaron states that, due to the long-range electron phonon interaction typical of ionic crystals, may extend over several lattice sites (large polarons). Large polarons can display band-like coherent transport with substantial mobility (>1 cm$^2$/Vs), that falls with increasing temperature. In this presentation, we will provide an overview of our recent theoretical and experimental studies on small and large polaron generation and relaxation dynamics in 2D and 3D perovskites.

4:00 PM ES15.16.02
Impact of Cation Composition on Polaron Formation and Charge Carrier Mobility in Perovskites

Andrei Petsiuk1, Hannes Hempel1, Martin Stolterfoth2, Pascal Becker1, Dieter Neher2, Rainer Eichberger1 and Thomas Unold1; "Helmholtz Zentrum Berlin, Berlin, Germany; "University of Potsdam, Berlin, Germany.

Perovskites exhibit excellent opto-electronic properties – apart from their rather moderate charge carrier mobilities. These low mobilities have been attributed to the formation of large polarons and dynamic disorder due to low energetic phonons. However, the prevalent Hellwarth-Feynman theory of polarons still overestimates the mobility by an order of magnitude and the limiting mechanism is still unclear. Here, we investigate the mismatch between polaron theory and observe mobilities by varying cation composition of perovskites. To this end, the charge carrier mobility and the optical phonon spectrum of XPO$_4$ perovskite thin films with different Cs, MA and FA composition are measured by time-resolved terahertz spectroscopy. The main phonon modes are observed for all samples at ca. 0.9 THz (30 cm$^{-1}$) and ca. 1.9 THz (63 cm$^{-1}$) and exhibit only minor shifts with cation composition. This observation supports the assignment of these main optical phonon modes to 1-ph vibrations on the anion lattice. The cation composition only slightly distorts the unit cell with minor impact on the I-Pb bond.

The measured charge carrier mobilities are in the range of 40-90 cm$^2$/Vs which further supports similar polaron formation for different cation compositions. The difference can be attributed to variations in the ionic screening with cation composition and to the microstructure of the samples.

Finally, we identify several reasons for the difference between measured mobilities and estimation by the Hellwarth-Feynman theory.

First, we find higher mobilities for lower photo-exciated charge carrier concentrations. The measured mobility on MAPbI$_3$ at low injection is 81 cm$^2$/Vs which is 2-3 times larger than typical literature values. This value is relatively close to the mobility of 230 cm$^2$/Vs which we estimated by the Hellwarth-Feynman theory.

Second, the observed phonon modes are mostly of transversal character, which are not considered in the mobility estimation by the Hellwarth-Feynman theory. The potential impact of such phonon modes on the mobility of halide perovskites will be discussed.

4:15 PM ES15.16.03
Interplay Between Structure and Physical Properties in Organic-Inorganic 2D Perovskites

Jean-Christophe Blancou1, Jacky Even2, Andreas Stier3, Claudine Katan1, Jared Crochet1 and Aditya Mohite2; "Los Alamos National Laboratory, Los Alamos, New Mexico, United States; "Rice University, Houston, Texas, United States; "Institut National des Sciences Appliquées, Rennes, France; "Technische Universität München, Garching, Germany; "Université de Rennes, Rennes, France.

Solution processed, organic-inorganic (hybrid) 2D perovskites have recently emerged as efficient semiconductors for light emission and photovoltaics, with technologically relevant stability [1]. Hybrid 2D perovskites feature unique structural characteristics related to the hybrid nature of their crystal lattice, which includes soft and dynamic lattice structure and organic-inorganic atom-thick interfaces. However, there is still little knowledge of the interplay between, on the one hand, the photo-excited states and electronic properties of hybrid perovskites and, on the other hand, the unique structural characteristics of this class of materials. Here, using optical spectroscopy and 60-Tesla magneto-absorption supported by modelling, we report the dependence of the formation, dynamics, and recombination of exciton states on the structural and compositional details of hybrid 2D perovskites. First, our work reveals that the exciton properties (reduced mass, binding energy, etc.) are tailored by both the thickness of the 2D perovskites and the size of the organic molecules in the lattice [2]. Second, our observations demonstrate the existence of unique electronic states located at the edges of the 2D perovskite layers [3], which are understood to result from local distortions of the lattice at the edges, and which promote exciton dissociation and localization [4]. Finally, we will discuss some of our recent results that provides insight into the hetero-coupling between hybrid 2D perovskites and graphene-like layers such as graphene and transition metal dichalcogenides.

Additionally, we have demonstrated the effect of Cl additives on ideality factors of our devices as well as lower recombination using impedance spectroscopy. Importantly, molecular engineering by applying chloride (Cl) additives greatly enhances the stability of the PSCs, which show only 5% degradation after aging for 90 days.

The presence of surface and grain boundary defects in organic–inorganic halide perovskite films is detrimental to both the performance and operational stability of perovskite solar cells (PSCs). Compositional engineering and surface treatment of perovskites are effective approaches to passivate these defects. Here, we study the effect of chloride additives on the bulk and surface defects of mixed-cation and halide PSCs. We found that using an anti-solvent technique, the perovskite film is divided into two separated layers, i.e., a bottom layer with large grains and a thin capping layer with small grains. The addition of formamidinium chloride (FACl) into the precursor solution removes the small-grained perovskite capping layer and suppresses the formation of bulk and surface defects, providing a perovskite film with remarkably enhanced crystallinity and large grain size up to over 1 μm. Time-resolved photoluminescence measurements show longer lifetimes for perovskite films modified by FACl and subsequently passivated by 1-Adamantylamine hydrochloride (ADAHCl) as compared to the reference sample. These treatments improve the film quality and enable a high PCE of 21.2% and $V_{oc}$ of 1152 mV with negligible hysteresis.

Importantly, molecular engineering by applying chloride (Cl) additives greatly enhances the stability of the PSCs, which show only 5% degradation after aging for 90 days. Additionally, we have demonstrated the effect of Cl additives on ideality factors of our devices as well as lower recombination using impedance spectroscopy.

**SYMSPOSIUM ES16**

**Perovskite Photovoltaics and Optoelectronics**

April 22 - April 26, 2019

**Symposium Organizers**

Antonio Abate, Helmholtz Berlin
Mingzhen Liu, University of Electronic Science and Technology
Michael Saliba, Adolphe Merkle Institute
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* Invited Paper

**SESSION ES16.01: Interfaces I**

Session Chairs: Antonio Abate and Michael Saliba

Monday Morning, April 22, 2019

PCC North, 100 Level, Room 125 AB

8:30 AM *ES16.01.01*

Understanding and Designing Interfaces and Defects in Perovskite Solar Cells

Juan-Pablo Correa-Baena; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Perovskite solar cells promise to yield efficiencies beyond 30% by further improving the quality of the materials and devices. Electronic defect passivation, and suppression of detrimental charge-carrier recombination at the different device interfaces has been used as a strategy to achieve high performance perovskite solar cells. In this presentation, I will discuss the role of electronic defects and how these can be passivated to improve charge-carrier lifetimes and to achieve high open-circuit voltages. I will discuss the characterization of 2D and 3D defects, such as grain boundaries, crystal surface defects, and precipitate formation within the films, by synchrotron-based techniques. The importance of interfaces and their contribution to detrimental recombination will also be discussed. As a result of these contributions to better understanding 2D and 3D defects, the perovskite solar cell field has been able to improve device performance. Albeit the rapid improvements in performance, there is still a need to improve these defects to push these solar cells beyond the current state-of-the-art.

9:00 AM *ES16.01.02*

Interface Modification and Molecular Engineering in the Perovskite Architecture Enable Highly Efficient, Stable and Electroluminescent Perovskite Solar Cells

Mohammad Mahdi Tavakoli; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Non-radiative recombination loss specially at the interfaces is a big challenge in the perovskite solar cells (PSCs) and affect the performance, stability, reproducibility of devices. Engineering the interfacial regions of the PSCs using an interface layer or additives is an effective strategy to address this issue. Our new findings report on a major breakthrough in the PSCs research. We discovered amazingly effective ways to mitigate the radiationless recombination of charge carriers at the interfaces of the perovskite with either electron transporting layer (ETL) or the hole transporting layer (HTL). In terms of ETL modification, we treat the surface of ETLs in the PSCs using SnO2 and graphene, results in drastically improved the charge transfer properties, retarded the recombination rate and reduced the unwanted interfacial reactions at the interfaces with perovskite film. Moreover, we found that incorporation of the molecular modulators such as adamantanes either at the interface of perovskite with HTL or into the HTL solution prevents non-radiative recombination drastically, resulting in a highly efficient and stable PSC. Based on these techniques, we achieved PSCs (for both planar and mesoporous structures) with electric to power conversion efficiency (PCE) of ~22%, an open circuit voltage of up to 1245 mV, external electroluminescence yield of 2.5% and a great operational stability, which are the records for triple A-cation PSCs with respect to the band gap (1.61 eV). Our proposed approaches open up a promising route for fabrication of cost-effective solar cell and pave the way for the development and commercialization of the PSCs.

9:30 AM *ES16.01.03*

Surface Defects of CH3NH3PbBr3 and Their Effect on Interfacial Device Properties

Collin Stecker1, Kexi Liu2, Jeremy Hieulle1, Zhenyu Liu2, Robin Ohmann1, Luis K. One1, Guofeng Wang1 and Yabing Qi1; 1Okinawa Institute of Science and Technology, Okinawa, Japan; 2Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.
Understanding defects in perovskite films is key to improving device performance and stability. It has been hypothesized that vacancy defects enable ion migration, which has been implicated to cause current-voltage hysteresis and long-term material degradation. Additionally, defects at the surface of the perovskite film may affect the interfaces in a device, and interface engineering is seen as an important avenue for improving device performance. Scanning tunneling microscopy (STM) offers the ability to probe the surface of OFPs with atomic resolution, including resolving individual vacancy defects. Scanning the same area multiple times allows for observation of dynamic events. Here, multiple types of defects were resolved and dynamic ion migration to and from the surface was imaged at the atomic scale. DFT calculations indicate vacancy defects are MABr vacancies and that vacancy defects at the surface of the film change the local work function, which has important implications for energy level alignment and charge transfer between layers in a photovoltaic device.

References
The efficiency of perovskite solar cells has skyrocketed from 3.8% to 23.3% in the past few years. For the best MAPbI$_3$ perovskites, the open-circuit voltage deficit, defined as the difference between bandgap and open-circuit voltage ($V_{oc}$), is only 0.37 V, approaching other best technologies such as GaAs [1]. However, similar to III-V materials, higher bandgap perovskites tend to have larger $V_{oc}$ deficits. For example, for 1.64-eV and 1.7-eV perovskites, the best $V_{oc}$-deficits are 0.49 V and 0.51 V, respectively [2]. This voltage loss limits the performance of wide-bandgap perovskites, and their applications on, for instance, tandem solar cells.

The $V_{oc}$ of photovoltaic devices is governed, hierarchically, by recombination in the absorber and the carrier-selective contacts of the devices. Grain engineering has been proven to be an effective way to reduce defect density and, thus, suppress recombination to enhance the $V_{oc}$ [2][3]. In our work, we focus on exploring different carrier-selective contact materials for perovskites.

With inverted architecture, we have replaced PTAA hole contact with boron-doped a-Si:H material. Our first device shows a $V_{oc}$ of 1.02 V on a 1.6-eV CsMAFABr perovskite, and 0.92 V on a 1.67-eV perovskite. These numbers are very close to the PTAA control devices with $V_{oc}$ of -1.1 V. Although the FF is rather poor due to shunts and possible large series resistance due to band misalignment. We are in the process of making new devices without shunts, and characterizing the band alignment between our a-Si:H hole contact and perovskite absorber. By the time we present, we believe we’ll have such information. In addition to the current-voltage measurement, we will use surface photovoltage and XPS/UPS etc technique to obtain the band information, and also use a Sun-Voc tool that we developed to probe the series-resistance-free fill factor of the device with a-Si:H contacts. We’ll also further employ phosphorous-doped a-Si:H as an electron contact to perovskite, and perform a thorough analysis on that as well.

Enhanced Transport and Carrier Selectivity at Perovskite Interfaces Enabled by Ordered Perylene Monolayers

Alexander D. Carl and Ronald L. Grimm; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

To maximize the scalable deployment of perovskite PV, we investigate low-temperature organic monolayer-based morphologies to chemically and electrically glue perovskites to their contacting phases while maintaining a “soft”, flexible interface and carrier selectivity. We have covalently grafted vertically oriented perylene diimide layers on TiO$_2$ through and inside linkage to a surface-bound silane. Secondary functionalization with a diamine to the terminal anhydride yields A-type cation moieties that serve as a chemical hook for perovskite deposition. UPS-quantified HOMO and LUMO levels of perylene diimide molecules aligned to facilitate electron transport to the TiO$_2$ substrate while blocking holes. Reflection- Absorption Infrared Spectroscopy (RAIRS) and X-ray photoelectron spectroscopy revealed a high coverage of vertically oriented perylene diimide. Perylene interfacial monolayers yield improved energy conversion relative to TiO$_2$ perovskite interfaces that we ascribe to enhanced interfacial carrier selectivity and transport, and reduced recombination. We discuss the present context in the results of other morphologies relevant to tandem photovoltaics.

1:30 PM Session ES16.02: Device Physics and Characterization

Session Chairs: Piers Barnes and Taiho Park

PCC North, 100 Level, Room 125 AB

What Can Impedance Spectroscopy Tell Us (for the Moment) About Perovskite Solar Cells?

Ivan Mora-Sero; Universitat Jaume I, Castello de la Plana, Spain.

Perovskite solar cells are surprising the photovoltaic community as unconventional behaviors have been reported. In most of the cases the origin of these behaviors is not completely understood and also, very important for the final application, how them influence the final performance of the device. On the other hand Impedance spectroscopy is a non-destructive characterization technique that can help in the understanding of these devices. Impedance spectroscopy is a characterization method in the frequency domain that allows to decouple physical processes with different characteristic times at the working conditions i.e. under illumination and applied bias. Despite the huge potentiality of this technique for the characterization of perovskite solar cell a complete model of impedance for this kind of cells applicable in all the conditions and configuration has been elusive for the moment. Undoubtedly, the combined action of electron and holes and ions in perovskite solar cell is at the base of the complex behavior observed in this kind of devices. In this talk we compare the well know dye sensitized solar cells with the perovskite solar cells highlighting similarities and differences. In addition the interest of impedance characterization of different types of perovskite solar cells is discussed.

2:00 PM Ionic-to-Electronic Current Amplification in Hybrid Perovskite Solar Cells—Ionically Gated Transistor-Interface Circuit Model Explains Hysteresis and Impedance of Mixed Conducting Devices

Davide Moia; Ilariu Gemetti; Phil Calado; William Fisher; Michael Stringer; Onkar Ganne; Yinghong He; Pablo Dencoso; David Lidzey; Emilio Palomares; Jenny Nelson and Piers Barnes; 'Physics, Imperial College London, London, United Kingdom; 'ICIQ, Tarragona, Spain; 'Physics, The University of Sheffield, Sheffield, United Kingdom; 'Chemistry, Ludwig-Maximilians-Universität München, Munich, Germany; 'School of Electrical and Electronic Engineering, Newcastle University, Newcastle, United Kingdom.

Mobile ions in hybrid perovskite semiconductors introduce a new degree of freedom to electronic devices suggesting applications beyond photovoltaics. An intuitive device model describing the interplay between ionic and electronic charge transfer is needed to unlock the full potential of the technology. We describe the perovskite-contact interfaces as transistors which couple ionic charge redistribution to energetic barriers controlling electronic injection and recombination. This reveals an amplification factor between the out of phase electronic current and the ionic current. Our findings suggest a strategy to design thin film electronic components with large, tuneable, capacitor-like and inductor-like characteristics. The resulting simple equivalent circuit model, which we verified with time-dependent drift-diffusion simulations of measured impedance spectra, allows a general description and interpretation of perovskite solar cell behaviour.

arXiv:1805.06446

Photo-induced phase separation has been reported for a range of mixed-halide perovskites, which limits the available band-gap energies for photovoltaic applications [1,2]. An enhanced understanding of the phase separation mechanism is essential to rationalize limitations and design stable perovskite semiconductors. Up to now, phase separation and segregation has been detected by means of X-ray diffraction (XRD), photoluminescence (PL) and cathodoluminescence experiments [3,4]. During electron microscope experiments, the electron beam may cause changes in halide perovskites [4, 5] and we here show that phase separation can be induced by electron beam irradiation of the sample. Inorganic CsPb(Br$_{3-x}$I$_x$)$_2$ thin films were deposited by spin-coating and the phase separation investigated in-situ by transmission electron microscopy (TEM). By this approach, it was possible to directly monitor the phase separation of CsPb(Br$_{3-x}$I$_x$)$_2$ thin films on the nanoscale into CsPbI$_3$ and CsPbBr$_3$ domains. We discuss the comparability of the interactions of electrons and photons with the halide-perovskite thin film and correlate the in-situ TEM with XRD and PL measurements of the same samples. Furthermore, we present different approaches of sample preparation for this in-situ TEM investigation.

Atomic Scale Analysis & Electronic Properties Characterization of MAPbI₃ Perovskite Material

Asfhan Jamshaid, Rohin Ohmann, Jeremy Hieulle, Collin Stecker, Luis K. Ono and Yabing Qi; EMSSU, Okinawa Institute of Science & Technology, Onna, Japan.

In recent years, the organic-inorganic hybrid perovskite has gained an increasing research interest in academia for applications in thin film solar cells, due to rapidly increased efficiency (from 3.8% to 23.3% within a decade) [1], high absorbance coefficient [2], low-cost fabrication process, and material availability [3]. Among the hybrid perovskites, MAPbI₃ (CH₃NH₃PbI₃) based solar cells have shown high conversion efficiency with several advantages, such as thermal instability, hysteresis loss at room temperature. Therefore, the commercialization of these solar cells is still a challenge. Understanding and resolving these issues necessitates the investigation of the sample at the atomic scale to determine the underlying fundamental processes. Here, we present the growth and experimental characterization of thin MAPbI₃ films on Au (111) under ultra-high vacuum conditions (UHV = 1x10⁻¹⁰ Torr). The thick films were prepared by vacuum evaporation of the precursor molecules MAI and PbI₂ with a thickness of a few monolayers (approx. 4 nm). We characterize the sample with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), obtaining information about the atomic structure, and chemical composition. For the electronic properties analysis, we used ultraviolet photoemission spectroscopy (UPS), and inverse photoemission spectroscopy (IPES). Our study will provide the basis for further understanding ion incorporation and stability at the atomic scale.

Understanding and the Modulation of the Interaction Between Electronic and Ionic Charge Transport at Hybrid Perovskite-Liquid Electrolyte Interface

Priya Srivastava and Monojit Bag; Institute of Technology Roorkee, Roorkee, India.

Manifested by high absorbance coefficient, large carrier diffusion length, ambipolar charge transport and moderate mobility of charge carriers, organo-lead halide perovskites recently emerged as a promising candidate for high efficiency and low-cost solution processed solar cells, needs no introduction. Perovskite Solar Cells (PSCs) have already gathered considerable attention, showing a tremendous hike in efficiency from 3.8% by Kojima et al. (2009) to 22.1% by Yang et al. (2017). A lot of research has been done on the efficiency improvement of PSCs by optimization of the film morphology at the interfaces by various characterization techniques including electrochemical impedance spectroscopy (EIS) in a solid-state active device geometry. Recently, the optimization of the film morphology at liquid electrolyte interface by EIS is trending as a more simplified approach. Li et al. have measured the flat band potential, density and type of charge carrier at the perovskite-liquid interface from Mott-Schottky plot for spin coated and spray coated films of methylammonium lead tri-iodide (MAPbI₃) perovskite. Srivastava et al. have optimized the morphology of MAPbI₃ perovskite thin films at liquid interface by controlling nucleation and growth during film fabrication by spin coating the films on the premed substrates. However, there is a need for understanding the charge transfer at these interfaces in more detail. Here, we have studied the kinetics of charge transfer and diffusion at the hybrid organic-inorganic perovskite-liquid electrolyte interface under the effect of applied bias. By applying the different dc bias from 0 to +1V and 0 to -1V, it was found that the ion diffusion at low frequency regime gets modulated due to charge accumulation. The charge transport resistance is initially increased to a maximum at around 0.4 V applied bias along with the decrease in the space charge capacitance. A transition state is observed around 0.4 V to 0.6 V due to the strong electronic-ionic interaction where charge transport resistance decreases and capacitance increases. However, at higher applied bias voltage charge transport resistance increases again and capacitance starts to decrease due to excess ion accumulation. The perovskite films show a similar trend of change in impedance under both positive and negative bias. The Mott-Schottky Plot for forward and reverse voltage scan shows n-type and p-type behavior which indicates the ambipolar nature of perovskite semiconductor. The significant difference in the impedance spectra can be seen in dark and light which is attributed to the high absorbance coefficient of the perovskite material. We have proposed a model to explain the charge kinetics across the perovskite-liquid electrolyte interface.

References

(4) Srivastava et.al have optimized the morphology of MAPbI₃ perovskite thin films at liquid interface by controlling nucleation and growth during film fabrication by spin coating the films on the premed substrates. However, there is a need for understanding the charge transfer at these interfaces in more detail. Here, we have studied the kinetics of charge transfer and diffusion at the hybrid organic-inorganic perovskite-liquid electrolyte interface under the effect of applied bias. By applying the different dc bias from 0 to +1V and 0 to -1V, it was found that the ion diffusion at low frequency regime gets modulated due to charge accumulation. The charge transport resistance is initially increased to a maximum at around 0.4 V applied bias along with the decrease in the space charge capacitance. A transition state is observed around 0.4 V to 0.6 V due to the strong electronic-ionic interaction where charge transport resistance decreases and capacitance increases. However, at higher applied bias voltage charge transport resistance increases again and capacitance starts to decrease due to excess ion accumulation. The perovskite films show a similar trend of change in impedance under both positive and negative bias. The Mott-Schottky Plot for forward and reverse voltage scan shows n-type and p-type behavior which indicates the ambipolar nature of perovskite semiconductor. The significant difference in the impedance spectra can be seen in dark and light which is attributed to the high absorbance coefficient of the perovskite material. We have proposed a model to explain the charge kinetics across the perovskite-liquid electrolyte interface.

3:00 PM BREAK

3:30 PM • ES16.02.06
Tandem Perovskite Architectures—Overcoming the Complexities of Halide Ion Exchange

Prashant V. Kamat, VikashKumar Ravi and Rebecca Scheidt; Radiation Laboratory, Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States.

Mixed halide lead perovskites offer a useful strategy for continuous tuning of semiconductor bandgap. Based on their tunable optical properties these mixed halides are being considered as attractive candidates to develop single junction and multijunction tandem solar cells. The ease of halide ion exchange property poses a problem to create a tandem structure with layers of metal halide perovskites of different compositions. In order to keep the lead halide perovskite nanocrystals intact without undergoing exchange of halide ion and retain the original band structure one needs to suppress the halide ion migration across the nanocrystals. We have now successfully achieved this task by capping CsPbBr₃ and CsPbI₂ nanocrystals with PbSO₄-Oleate. Absorption measurements show that the nanocrystal assemblies maintain their identity as either CsPbBr₃ or CsPbI₂, for several days. Furthermore, we have electrochemically deposited these assemblies as hierarchical structures on electrode surfaces and employ them in light emitting devices. The effectiveness of PbSO₄-Oleate capping of lead halide perovskite nanocrystals offers new opportunities to overcome the challenges of halide ion exchange and aid towards the tandem design of perovskite light harvesting assemblies.

4:00 PM • ES16.02.07
Characterisation of Electron Beam Induced Damage in Multi-Cation and -Anion Perovskite Solar Cells During Electron Microscopy

Ashilan Babagyi, Mohit Raghuvanshi, Bert Conings, Frank Renner, Oana Cociocaru-Mirédin and Hans-Georg Boyen; 1 Institute for Materials Research (IMO-IMOMEC), Diepenbeek, Belgium; 2RWTH Aachen University, Aachen, Germany.

Metal halide perovskites have sparked tremendous enthusiasm in the photovoltaic community with their promising performances. Currently holding a record power conversion efficiency of 23.3%, this exciting material class is approaching the mighty Si-powerhouse, concurrently opening encouraging avenues in (all-) perovskite multi-junction applications while approaching commercial exploitation. At the origin of these highly performing devices lie superior absorber properties that so far have been investigated by a plethora of characterisation techniques. Amongst all, electron microscopy (EM) remains one of the most extensively employed tools for studying the absorber in terms of crystallography, morphology and interfaces, lattice defects, compositions, and charge carrier lifetimes but with severe obstacles such as thermal instability, hysteresis loss at room temperature. However, a crucial challenge upon using EM remains the beam sensitivity of the absorber, especially upon imaging with an increased electron dose. Resulting in structural and chemical changes in the light harvester in function of the total electron dose, it becomes extremely challenging to validate obtained results and those reported in literature. Therefore, a quantitative characterisation of the beam damage is highly necessary to avoid, or at least mitigate, changes to the sample upon imaging in future analysis. Therefore, in this work, we investigate the current degeneration in multi-cation and -anion perovskite solar cells in function of the total electron dose by means of electron beam induced current (EBIC) measurements on rough cross-section of corresponding devices—providing an indirect yet quantitative route to characterise the electron beam induced damage to the absorber. Allowing the extraction of current decay profiles, various compositional perovskites are compared in terms of beam sensitivity, and operational parameters are indicated to avert (or at least mitigate) sample damage during imaging.
Halide perovskite solar cells (HPSCs) present a cutting-edge nanotechnology which has demonstrated remarkable power conversion efficiency increases to a recently reported value of 23% [1]. The high efficiency combined with low-cost production make HPSCs one of the most promising solar cell technologies but significant challenges related to their stability are yet to be solved. Exposure to oxygen, humidity, temperature, atmospheric pressure and UV light stimulates a complex set of degradation mechanisms such as diffusion of molecular oxygen and water, interfaces and the active material degradation, electrode reaction with the organic material to morphological and macroscopic changes [2]. For this reason, devices are encapsulated which prolongs their life and also increases mechanical stability [3]. As the natures and timescales for each of these chemical reactions differ, it is challenging to elucidate the degradation processes. Secondary ion mass spectrometry (SIMS) is one of the few techniques that can offer valuable insights into potential degradation mechanisms by obtaining spatially resolved chemical analysis of organic and inorganic layers and interfaces. In this work, we present the high mass-resolving power depth profiling of HPSCs using the 3D OrbiSIMS [4].

The 3D OrbiSIMS comprises dual beam and dual analyser configuration by integrating a Q Exactive™ HF Hybrid Quadrupole-Orbitrap™ mass spectrometer with a high-resolution imaging ToF-SIMS platform. Advantages of this instrument include a significantly higher duty cycle compared with time-of-flight instruments (using pulsed ion beams), high-mass resolving power (>240,000) and high-mass accuracy (~ 1 ppm), up to 4 orders of magnitude dynamic range for organic materials and the ability to do MS/MS. Here, we apply single beam depth profiling combined with high-mass resolving power to study the interface and interlayer chemistry in HPSCs and the degradation mechanisms that occur when exposed to air. Critical to achieving this is air-free transfer between a sample preparation glovebox and the 3D OrbiSIMS instrument. The air-free transfer protocol will be presented in this work.


5:30 PM ES16.02.09 Probing the Enhanced Stability of 2D Perovskite Solar Cell Materials Bryan Wygant, C. B. Mullins, Andrei Dolocan, David M. Abbott, Quyen Vu and Alexandre Ye; University of Texas at Austin, Austin, Texas, United States.

Organolead halide perovskites are a new class of photovoltaic materials for potential use in thin film solar cells, but suffer from rapid degradation under light and humidity, limiting their viability. Recently developed quasi-2D Ruddlesden-Popper phase perovskites show improved stability but, at present, the mechanism behind the stability is poorly understood. Here, we have used time-of-flight secondary ion mass spectrometry (ToF-SIMS), photoluminescence spectroscopy (PL), electrochemistry, and other techniques to study the chemistry and performance of 2D and 3D phases of methylammonium lead triiodide (MAPI) solar cells as a function of humidity exposure. ToF-SIMS depth profiles of both 2D and 3D MAPI planar solar devices (n-i-p, Cu/Perovskite/PEDOT:PSS) show the formation of a significant hydrolysis-based degradation layer at the surface of only 3D MAPI devices after humidity exposure. Isotopic D₂O studies confirm the layer is caused by ambient humidity, while electrochemistry confirms it is directly related to loss of cell performance. The growth of this hydrolysis layer is found to be inhibited in 2D MAPI devices by the formation of a thin protective layer composed of more thermodynamically-stable 2D phases, clearly observed in PL spectra, which protects the less stable 2D bulk. To confirm that this newly formed 2D layer improves stability, we created solar cells consisting of 3D MAPI films coated with a thin layer of the 2D perovskite, and show that these cells are more stable than un-treated 3D MAPI devices. As a result, we conclude that using 2D perovskite as a protective interface may be a simple way to improve device stability.

10:30 AM *ES16.03.01/ES15.01.01/ES17.03.01 Present Status and Next Important Challenge of Perovskite Photovoltaics Towards Industrialization Tsutomu Miyasaka; Toin University of Yokohama, Yokohama, Japan.

Power conversion efficiency (PCE) of lead halide perovskite solar cell (over 23%) has surpassed those of CIGS and CdTe, approaching the top value of crystalline Si cell. Our group has been able to achieve PCE over 21% by low cost ambient fabrication. However, high PCE of single-cell enabled by lead halide-based perovskite absorbers are now being saturated, taking the Shockley–Queisser (SQ) limit of open-circuit voltage (V_{OC}) (ca.1.32V) into account. Tandem cell making, which can further increases PCE up to 28% or more, leads to higher material and process cost and will raise a question if performance/cost ratio can be accepted in industry. Therefore, a smart way is to create a single cell which has high PCE comparable with that of GaAs (>28%) by reducing bandgap energy to <1.4 eV without accompaniment of increase in V_{OC}. This possibility will bring in a family of metal halide perovskites out of those depending on use of lead. In addition to such efficiency issue, high performance of organo lead halide materials is not compatible with robust high stability required for practical use. Ensuring the intrinsic thermal stability (desirably >200°C) of the perovskites is a key issue before industrialization. In addition, toxicity of lead-based perovskites are going to become the most formidable challenges for real use (commercialization), in particular, for applications to IoT society, which is one of the most promising field of perovskite photovoltaic device in terms of high voltage output even under weak illumination. These thoughts urge us to concentrate our next research of perovskite photovoltaics (PV) more on development of non-lead high efficiency absorbers. Sn perovskite is still a strong candidate because Sn(II) has been found to be stabilized against ambient air by metal doping method (such as Ge). Regarding Bi-based perovskites, we found AgBiI₃ as a promising all-inorganic absorber having high thermal and moisture stability. Stability also highly depends on the property of charge transport materials (CTMs), especially, the kind of hole transporter. Spiro-OMeTAD does not work at high temperature while P3HT, for example, is thermally stable. In our collaboration with JAXA, P3HT-based perovskite devices showed robust stability by exposure to high (100°C) and low (<40°C) temperatures and also to high energy particle radiations (Science, 2018, 2, 148). Selection of CTMs is another important key in combination with non-lead perovskite materials. In conclusion, next direction of perovskite PV should be to enhance PV performance of non-lead all-inorganic semiconductor materials by extended compositional engineering, in parallel with developing thermally stable CTMs. Our on-going studies on non-lead perovskite materials in our group will be introduced in the talk.
Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable band gaps and relatively benign defects and grain boundaries for systems based on Group 14 metals (e.g., Ge, Sn and Pb) [2]. Indeed, these materials have enabled unprecedented rapid improvement in perovskite photovoltaic performance to levels above 20% power conversion efficiency and with open circuit voltages above 1V for a single junction photovoltaic (PV) device [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility [4,5], semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.


SESSION ES16.04: Stability and Testing
Session Chairs: Jinsong Huang and Yabing Qi
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 125 AB

1:30 PM *ES16.04.01
Compositional and Interface Engineering of Perovskite Solar Cells
Anders Hafelielb; Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 22% with a mixed composition of iodide/bromide and organic and inorganic cations. With the use of SnO2 compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20%. Through the compositional engineering larger perovskite grains grown in a monolithic manner are observed and reproducibility and device stability have been improved. With regards to lifetime testing, we have shown a promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests.

2:00 PM *ES16.04.02
Degradation Mechanisms of Lead Halide Perovskite Solar Cells and Stability Improvement Strategies
Yabing Qi; Okinawa Institute of Science and Technology, Okinawa, Japan.

Perovskite solar cell research continues to progress rapidly on various fronts. My group at OIST is making efforts to use surface science and advanced material characterization to obtain in-depth understanding about perovskite materials and solar cells [1]. In this talk, I will present our research progress on understanding the degradation mechanism of perovskite materials [2,3] as well as developing strategies to improve stability of perovskite solar cells [4-6].


2:30 PM ES16.04.03
Thermally Stable, Planar Hybrid Perovskite Solar Cells with High Efficiency
Taiho Park; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Tin oxide (SnO2) is a promising material for the electron transport layer in planar perovskite solar cells (P-PSCs) due to its suitable energy level and high electron mobility. SnO2-based P-PSCs show the highest power conversion efficiency among planar structure devices, but the PCE remains still low compared to the mesoporous TiO2-based PSCs and there is a lack of thermal stability study. In this study, we develop a simple interface engineering to improve optoelectronic properties and the thermal stability of the P-PSCs. The modified SnO2 shows high conductivity, effective charge extraction ability and high recombination resistance. Empirically, efficiencies of 21.43% and 20.5% were reached for the device with doped Spiro-OMeTAD and with dopant-free asy-PBTBDT, respectively, in the present study. The devices with modified SnO2 show excellent stability under mild (humidity of 25%) and harsh conditions (humidity of 85%; temperature of 85°C). Thus, our newly developed method guarantees highly efficient and thermal stable P-PSCs.

2:45 PM ES16.04.04
Highly Efficient and Stable Perovskite Solar Cells via Perovskite Surface Modification
Zhifang Wu and Yabing Qi; Okinawa Institute of Science and Technology, Okinawa, Japan.

Organic-inorganic hybrid perovskite solar cells show the promises as the next-generation photovoltaic technology. The efficiency has quickly increased from 3.8% [1] to 23.2% since 2009. [2] However, instability of perovskite solar cell is a big issue hindering its commercialization and practical applications. By combining thermal-insensitive organic-inorganic perovskite and moisture-resistant electrode, we report successful fabrication of stable organic-inorganic hybrid PSCs which shows enhances stability under tough aging condition. Surface contact is another critical factor affecting solar cell efficiency. After suitable surface modification, solar cell efficiency is significantly improved from 12.2% to 14.9%.


3:00 PM BREAK

3:30 PM ES16.04.05
Engineering Stress in Perovskite Solar Cells to Improve Stability
Nicholas Rolston1, Kevin A. Bush1, Adam Printz1, Aryeh Gold-Parker1, 2, Michael D. McGehee1, Michael F. Toney1, 2 and Reinhold H. Dauskardt1; 1Stanford University, Stanford, California, United States; 2SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Metal halide perovskites hold tremendous promise for next-generation solar cells, more than any other recently developed low-cost active PV material. To fulfill this promise, perovskites must first overcome the chemical and thermomechanical instability that has long been observed in them. While some promising results have recently been achieved in scalability with power conversion efficiencies (PCE) of 12% for 100 cm² perovskite devices, the thermomechanical instability of perovskites remains a significant challenge to producing module-scale perovskite solar cells with operational lifetimes comparable to c-Si and CdTe.

In particular, stresses are generated in perovskite films during processing and magnified in service by environmental effects such as thermal cycling, resulting in the formation of
defects and propagation of fracture and delamination. Additionally, cracks that develop in the film are a source of accelerated degradation for the transport of gases, moisture, and other environmental species. Unfortunately, perovskite layers are exceptionally fragile and susceptible to delamination as measured by their fracture energy—less robust than organic photovoltaics (OPVs) by an order of magnitude and c-Si or copper indium gallium diselenide (CIGS) solar cells by two orders of magnitude. Despite the significance of film stresses for device stability, the origin and magnitude of stresses in perovskite films have been largely overlooked. In addition to causing fracture, stress accelerates the rate of photocatalytic degradation in many materials—such as fuel cells, microelectronics, and photovoltaics—and a recent report shows that perovskite are no exception.

Perovskites can accumulate residual stresses during processing through several pathways. For example, in solar cell devices, perovskites have much higher coefficients of thermal expansion (CTE) than the other device layers and the glass substrate. When perovskites are annealed after deposition and subsequently cooled back to room temperature, a lower-CTE substrate constrains the perovskite from contracting, an effect that generates lattice strain in the film. Given the extreme mechanical fragility of perovskite films, and for further stress development during fabrication and operation (e.g., exposure to environmental stressors such as thermal cycling), these residual stresses could contribute significantly to light, heat, and moisture-based chemical degradation as well as fracture in devices.

In this work, we report on an overlooked factor affecting stability: the residual stresses in perovskite films, which are tensile and can exceed 50 MPa in magnitude, a value high enough to deform copper. These stresses provide a significant driving force for fracture. Films are shown to be more unstable under tensile stress—and conversely more stable under compressive stress—when exposed to heat or humidity. Increasing the formation temperature of perovskite films directly correlates with larger residual stresses, a result of the high thermal expansion coefficient of perovskites. Specifically, this tensile stress forms upon cooling to room temperature, as the substrate constrains the perovskite from shrinking. No evidence of stress relaxation is observed, with the purely elastic film stress attributed to the thermal expansion mismatch between the perovskite and substrate. Additionally, the authors demonstrate that using a bath conversion method to form the perovskite film at room temperature leads to lower stress values that are unaffected by further annealing, indicating complete perovskite formation prior to annealing. It is concluded that reducing the film stress is a novel method for improving perovskite stability, which can be accomplished by lowering formation temperatures, flexible substrates with high thermal expansion coefficients, and externally applied compressive stress after fabrication.

In the current work, CSN testing is used to measure the interface delamination in perovskite and silicon/perovskite tandem solar cells (SPTS), which could lead to lowering of the fill factor (FF) under operating conditions of solar cells. In this test configuration, nanoindentation is performed on the substrate which is typically ~5–20 μm away from the electrode to air interface. The load-displacement curve obtained from the nanoindentation testing will be used to determine the fracture energy with the aid of a semi-quantitative analytical model to compute and compare adhesion and mechanical properties of samples with different interfaces.[2] At the conference, details pertaining to the CSN test and subsequent analytical analysis to get the fracture energy will be presented for various configurations of perovskite solar cells.

References


4:00 PM ES16.04.07

Comprehensive Multifactorial Studies on the Degradation of Perovskite Solar Cells in Operation Carlos Biaou, Matt McPhail, Vivek Subramanian and Oscar Dubon; University of California, Berkeley, Berkeley, California, United States.

The issue of long-term stability in perovskite solar cells under atmospheric conditions remains at the forefront of making them viable technologies. To facilitate a firm understanding of the processes at stake and their influence, it is important to employ a systematic investigation of degradation [1]. The interactions between various degradation phenomena (e.g. the effect of load, atmosphere, etc.) can be substantial, warranting the use of multifactorial methodologies to extract dominant effects and their interactions. As such, we use a design of experiments (DOE) methodology, which allows us to identify salient confluent factors and their interactions as they affect the operation of the solar cells. Specifically, we observe the influence of the combination of temperature, humidity, perovskite type, and loading condition on electrical (I-V), crystallographic (XRD), and optical (UV-Vis) characteristics. We also track their impact on the concentration and activation energy of deep level traps in CsxFA1-xPbI3 and MAPbI3 solar cells as a function of degradation via photo-induced conductivity transient spectroscopy. This study thus constitutes a framework upon which we can further our mechanistic understanding of degradation in perovskite solar cells.

Reference

4:15 PM ES16.04.08

Damage-Free Deposition of Transparent Conducting Oxide on Perovskite Solar Cells Shalinee Kadavady1, Jonathan L. Bryan1, Yuji Okamoto2,3 and Zachary Holman1; 1Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, Arizona, United States; 2University of Tsukuba, Tsukuba, Japan.

The wide and tunable bandgap of perovskites makes them attractive for use in tandem solar cells either as a top cell in perovskite/silicon and perovskite/thin film solar cells or as both top and bottom cells in all-perovskite tandem solar cells. For a tandem device, a transparent conducting electrode must be deposited on top of the perovskite solar cell to allow light transmission into the device. The conventional technique to deposit transparent conductive oxide (TCO) materials is sputtering. However, the high kinetic energy of the sputtered atoms and the UV radiation damages underlying layers of the cells (mainly the perovskite and hole contact layers), resulting in an S-shaped or shunted I-V curve with poor cell performance. Previously, a thin protective buffer layer of MoOx or SnO2 has been used before sputtering TCO, which places several processing constraints such as low-temperature deposition of both buffer layers, high transparency of the buffer layer, and appropriate energy level alignment.

In this work, an aerosol-based technique is developed to deposit a uniform TCO thin film on perovskite solar cells without any damage to the other layers of the cell. The technique involves a two-step spraying process. In the first step, a colloidal solution of indium tin oxide (ITO) nanoparticles is sprayed through an ultrasonic atomizer nozzle generating droplets containing nanoparticles. Once the solvent from the droplet evaporates, in the second step, the dry nanoparticles are passed through a fine orifice nozzle along with a carrier gas, creating a spray of nanoparticles which then deposit on the substrate. The pressure downstream the orifice nozzle is almost 10-fold lower than the upstream pressure,
which reduces the drag force on the fine nanoparticles and enables them to deposit on the substrate by impaction rather than flowing away along with the carrier gas. The absence of energetic atoms and radiation makes this technique suitable to deposit any kind of nanoparticle layer on top of perovskites without damage. The presentation will discuss this novel technique and its application in depositing a uniform layer of ITO nanoparticles as a top electrode in perovskite-based tandem solar cells to further boost their efficiency.

References:

4:30 PM ES16.04.09
Methylammonium-Free, High-Performance and Stable Perovskite Solar Cells on a Planar Architecture Silver-Hamill Turren-Cruz1, Anders Hagfeldt2 and Michael Saliba3; 1Institut fur Silizium Photovoltaik, Helmholtz Zentrum Berlin, Berlin, Germany; 2Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland; 3Adolphe Merkle Institute, Fribourg, Switzerland.

Currently, perovskite solar cells (PSCs) with high performances greater than 20% contain bromine (Br), causing a suboptimal bandgap, and the thermally unstable methylammonium (MA) molecule. Avoiding Br and especially MA can therefore result in more optimal bandgaps and stable perovskites. We show that inorganic cation tuning, using rubidium and cesium, enables highly crystalline formamidinium-based perovskites without Br or MA. On a conventional, planar device architecture, using polymeric interlayers at the electron- and hole-transporting interface, we demonstrate an efficiency of 20.35% (stabilized), one of the highest for MA-free perovskites, with a drastically improved stability reached without the stabilizing influence of mesoporous interlayers. The perovskite is not heated beyond 100°C. Going MA-free is a new direction for perovskites that are inherently stable and compatible with tandem or flexible substrates, which are the main routes commercializing PSCs.

SESSION ES16.05: Poster Session I
Tuesday Afternoon, April 23, 2019
5:00 PM – 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES16.05.01
A Facile Route to Grain Morphology Controllable Perovskite Thin Films Towards Highly Efficient Perovskite Solar Cells Funguo Zhang1, Jiayan Cong1, Yuanyuan Li1 and Licheng Sun1,2; 1KTH Royal Institute of Technology, Stockholm, Sweden; 2Dalian University of Technology, Dalian, China.

Perovskite photovoltaics have recently attracted extensive attention due to their unprecedented high power conversion efficiencies (PCEs) in combination with primitive manufacturing conditions. However, the inherent polycrystalline nature of perovskite films renders an exceptional density of structural defects, especially at the grain boundaries (GBs) and film surfaces, representing a key challenge that impedes the further performance improvement of perovskite solar cells (PSCs) and large solar module ambitions towards commercialization. Here, a facile strategy is presented utilizing a novel ethylammonium chloride additive to achieve high-quality methylammonium lead iodide (MAPbI3) films. Well-oriented, micron-sized grains were observed, which contribute to an extended carrier lifetime and reduced trap density without compromising for solar cell applications beneficial bandgap of the films. This additive engineering is demonstrated to boost the power conversion efficiency (PCE) to 20.9% and 19.0% for devices with effective areas of 0.126 cm2 and 1.020 cm2, respectively, with negligible current hysteresis and enhanced stability. Besides, perovskite films with a size of 10×10 cm2, and an assembled 16 cm2 (5×5 cm2 module) perovskite solar module with a PCE of over 11% were constructed.

ES16.05.02
Interface Induced Vertical Phase Separation for Economical, Efficient and Stable Perovskite Solar Cell—A Universal Strategy Simplifying the Device Preparation Process Jianxing Xia, Junsheng Luo, Fei Han, Zhongquan Wan, Yu Shi and Chunyang Jia; School of Electronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, China.

The major obstacles delaying the large scale commercialization of thin film solar cells based on hybrid organic halide perovskite are the complicated multi-step fabrication process, expensive materials, and environment and ion migration induced instability in the devices. In this research, we present a simple film-cover strategy to deposit light absorption layers (LALs) and hole transporting layers (HTLs) on a large area (4 x 4 cm2) through a single step process which is fundamentally based on polar and nonpolar interfacial induced self-vertical phase separation between perovskite and HTLs. This process is highly saving material which is 3% Spiro-OMeTAD and 7.5% perovskite used compared to the traditional spin-coating process, it is dozens of times for the cost saving. Moreover, The specific gradient phase separation construction based on the doped-free Spiro-OMeTAD shows specific energy level and device construction, leading to efficient carrier transportation and higher power conversion efficiency (PCE). We further systematically studied the origin of stability in this phase separated film compared to the traditional layer by layer spin-coating film, it suggested that the gradient HTLs embed in perovskite crystal boundary which can effectively restrain ion migrate and moisture at the crystal boundary, providing an excellent environmental stability and retains 95% of the initial efficiency even after 68 days being stored in ambient condition without encapsulation. We believe that our strategy will pave a new way for simple, economical, efficient, stable, large-area and commercialized perovskite solar cells (PSCs) preparation, and provide more understanding on the nature of ion migrate in the PSCs devices.

ES16.05.03
Single-Step Solution-Processed CH3NH3PbBr3 Perovskite Active Layer for Enhanced Efficiency of Light-Emitting Diodes Musunik Oh, Bhaskar Parida, Seonghoon Jeong, Keum-jin Ko, Jae-Wook Kang and Hyunsoo Kim; Chonbuk National Univ, Jeonju, Korea (the Republic of).

Organic-inorganic hybrid perovskites are emerging as highly attractive materials for optoelectronic applications due to their high color purity, broadly tunable optical bandgap, facile solution process, and efficient narrow band emission. Due to these features of merits, perovskite materials are highly utilized in the field of light-emitting diodes (LEDs) used as an active layer and have been successfully demonstrated to overcome the disadvantages of organic LEDs such as complex synthesis procedure, poor color purity, and high-cost processing. Because of these efforts, perovskite LEDs have recently reached external quantum efficiencies (EQEs) about 10 % for green and near-infrared emissions through the grain size of the perovskite active layer. However, it still has the problem that increase the number of grain boundaries causing exciton quenching and nonradiative recombination, while reduce the grain size of the perovskites.

In this study, we investigated single-step solution-processed methylammonium lead-bromide (CH3NH3PbBr3, MAPbBr3) perovskite active layer for enhanced efficiency of LEDs. The single-step process contributed to strong exciton confinement inside the perovskite grain for improves the radiative recombination of the LEDs by achieving small grain size through a nanocrystal pinning method. In addition, the single-stepped perovskites can effectively reduce exciton quenching to the metallic Pb atoms by passivating the perovskite grain boundaries due to the MABr-rich molar proportion. As a result, the LED fabricated with single-step-processed MAPbBr3 perovskite active layer (SSP LED) exhibited 33.8 % stronger maximum luminance (202 cd/m2) and 17.6 % higher EQE (4.0 %) compared to LED fabricated with double-stepped perovskites (DSP LED). The SSP LED also showed a 11.5 % reduction in series resistance (1.31 Ωcm2) and a 7.3 % improvement in current efficiency (9.53 cdA−) compared to DSP LED, which was attributed to reduced Joule-heating than the double-stepped perovskite layer. The both LEDs consisting of ITO/PEDOT:PSS/MAPbBr3/PCBM/Ag structures with a peak emission wavelength of 538 nm.

ES16.05.04
Interface Control for Perovskite Solar Cells Using GaN Thin Film Deposited by PEALD Huixun Wei, Peng Qiu, Mingzeng Peng and Xintie Zheng; University of Science and Technology Beijing, Beijing, China.

In a perovskite solar cell (PSC), charge generation, transport and collection layers are stacked together, producing several interfaces, which have significant influences on the charge processes. At present, the interfaces in PSCs have been carefully manipulated by controlling the compositions, or introducing interfacial buffers and passivation layers.
Here, unlike the widely-reported electron transport layers (ETLs) consisting of monolayer or multilayer metal oxide (TiO$_2$, ZrO$_2$, SnO$_2$, etc.), group-III nitride GaN work as ETL is explored to improve the electron transport and interfacial property. Benefiting from the self-limiting reactions of plasma enhanced atomic layer deposition (PEALD), the GaN thin films are conformal and pin-hole free with an accurate thickness control (<10 nm), which thus in favor of the deposition of high quality perovskite film on GaN and suppression of charge recombination between GaN and perovskite layers. The results indicate that GaN thin-film thickness have significant effects on the electron transport and collection of the photovoltaic cells, and the devices based on a 5 mm thick GaN ETL can achieve the highest cell efficiency of 15.18% with $J_{sc}$ of 22.56 mA/cm$^2$, $V_{oc}$ of 0.977 V and $FF$ of 0.689.

**ES16.05.05**

**Dion-Jacobson Type Tin-Based Halide Perovskite Solar Cells**

Min Chen, Zhenghong Dai, Yuanyuan Zhou and Nitin P. Padture; Brown University, Providence, Rhode Island, United States.

Perovskite solar cells (PSCs) based on lead-based halide perovskites (MAPbI$_3$, FAPbI$_3$, etc.) have achieved surprisingly high power conversion efficiencies (PCEs). However, lead-toxicity and intrinsic instability of these PSCs are major hurdles in the path towards the commercialization of PSCs. Typically, lead-free PSCs suffer from the low PCE (<10%) and poor stability. Therefore, we introduce a series of Dion-Jacobson type 2D tin-based perovskite materials, and realized a promising PCE of up to 4.5% in hole-transport-layer-free PSCs. These PSCs show high stability, with >10% PCE decay after 200 hours under continuous one-sun illumination. Thus, this work provides a new direction in the design and development of stable Sn-based perovskite solar cells.

**ES16.05.06**

**Water Effect on Cesium Doped Triple-Cation Hybrid Perovskite Solar Cells**

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The effect of water on the performance of perovskite solar cells has been intensively studied in recent years. However, the conflicting conclusion derived from different studies makes it impossible to fully understand the mechanism involved. Besides, all studies on water effect thus far have concentrated on single methylammonium cation perovskite materials. As a consequence, the effects of water on formamidinium and cesium perovskites are still unclear. Herein, we introduce water during the fabrication of triple-cation formamidinium and cesium based perovskites (abbreviated as Cs/FA/MA). By carefully controlling the water content, we demonstrate that water additive plays a significant role on the crystallization of the hybrid Cs/FA/MA perovskite film. More interestingly, the studies of the optical properties of the films indicate that water content determines the phase of the perovskites. Further, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) characterizations are applied to analyze the components and the chemical environments of the films. Finally, By finely tuning the concentration of water, a more stable device with a significant enhancement in PCE could be fabricated. The findings in this work contribute to the understanding of the effect of water on hybrid perovskites. It is suggested that further theoretical and experimental studies should be carried out to gain full understanding of the mechanism of water on hybrid perovskites.

**ES16.05.07**

**Grain-Boundary Functionalization for Highly Stable and Efficient Perovskite Solar Cells Based on Formamidinium Lead Iodide**

Zhenghong Dai, Yuanyuan Zhou and Nitin P. Padture; School of Engineering, Brown University, Providence, Rhode Island, United States.

Formamidinium lead iodide (FAPbI$_3$) perovskites have great potential for their used in perovskite solar cells (PSCs) due to their near-ideal bandgaps. However, FAPbI$_3$ perovskite (α-phase) tends to crystallize in a hexagonal non-perovskite structure (δ-phase) at room temperature which is thermodynamically more stable yet photo-inactive. Herein, we report a novel method to stabilize the α-phase FAPbI$_3$ via chemical functionalization of grain boundaries. By protecting the α-phase FAPbI$_3$ from the ingress of moisture from the atmosphere, the resulting PSCs show significantly improved stability. This method also boosts the power conversion efficiency by affording higher phase-purity of as-crystallized α-phase FAPbI$_3$ and defects passivation. This work points to a new route for designing high-performance PSCs with long-term durability.

**ES16.05.08**

**Strategic Synthesis of Ultra- Small NiCoO$_2$ NPs as Hole Transport Layer for Highly Efficient Perovskite Solar Cells**

Onyung Dan, Junyan Xiao, Fei Ye, Zhanfeng Huang, Hong Zhang, Lu Zhu, Jian Chen and Wallace C. Choy; Hong Kong University, Hong Kong, Hong Kong.

In this work, we synthesize ultra-small ternary oxide nanoparticles (NPs), NiCoO$_2$, by a novel strategy of controllable deamination of Co-NH$_3$ complexes in a system containing Ni(OH)$_2$. Through this approach, 5 nm NiCoO$_2$ NPs without exotic ligands are obtained and could be dispersed well in aqueous, which enables the formation of uniform and pin-hole free films. We apply the tightly covered NiCoO$_2$ film as hole transport layer in perovskite solar cells, and the corresponding devices reach a high power conversion efficiency of 18.23% and a promising stability (maintained ~90% PCE after 500 h light soaking) due to the formation of large perovskite grains and the reduction of film defects [1]. Besides improving device performance and stability, the newly synthesized NiCoO$_2$ film with the interesting features of low-cost, low-temperature, simple and green solution process expose the opportunities of ternary oxides for the applications of emerging photovoltaic devices. To the best of our knowledge, it is the first time that spinel NiCoO$_2$ NPs are applied as hole transport layer in perovskite solar cells successfully. In summary, this work not only demonstrates the potential applications of ternary oxide NiCoO$_2$ as HTLs in PVSCs but also provides an insight into the design and synthesis of ultra-small and ligand-free NPs HTLs to enable cost-effective photovoltaic devices.

**ES16.05.09**

**Suppressing Phase Segregation of Mixed-Halide Perovskite for Highly Light-Stable Perovskite/Perovskite/Si Multi-Junction Tandem Solar Cells**

Su Geun Ji, Ik Jae Park, Deok Ki Cho and Jin Young Kim; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

During the last years, inorganic-organic hybrid perovskite materials have been received attention as next-generation photovoltaics because of its excellent photovoltaic properties for solar cells. Currently, the power conversion efficiency (PCE) of single-junction perovskite solar cells has raised to 23.3% within a short period. In addition, double-junction tandem solar cells with perovskite materials have been developed such as perovskite/Si, perovskite/thin-film and perovskite/perovskite. The monolithic perovskite/Si tandem cells with double-side textured silicon substrate exhibit the PCE of 25.2%. However, realizing an efficient and stable perovskite-based triple-junction tandem solar cell remains challenging despite their very high theoretical PCE (~49%). The critical issue is the poor stability of perovskite solar cell against the light because large bandgap perovskite (over 1.9 eV) with mixed halide could be easily segregated to I-rich and Br-rich material under the continuous light. For a highly efficient and stable triple-junction tandem solar cells, therefore, the perovskite absorber that exhibits the highly stable under the operating condition is essential.

Here, we report a highly durable large bandgap (1.9 eV) perovskite solar cell under continuous light. Perovskite absorber containing triple cation (FA/MA/Sc) was prepared by two-step sequential deposition method. We added trimethylaluminum triacrylate (TMTA) as an additive into perovskite layer and cross-linked it by annealing process. By photoluminescence and X-ray diffraction analyses, we confirmed that a TMTA additive retarded the phase segregation of mixed halide. We assumed that the additive prevents the ion migration at the grain boundaries, which improves the light stability. As a result, the devices with the additive-added perovskite exhibited outstanding stability under continuous light with negligible PCE drop during 1 hour in ambient condition. Finally, we successfully fabricated solution process-based perovskite/perovskite/Si/mono-junction tandem solar cells on one-side textured Si substrates.

**ES16.05.10**

**The Influence of Guanidinium Cations on the Performance of Perovskites Solar Cells**

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Perovskites solar cells (PSCs) showed a dramatic improvement in their power conversion efficiencies (PCE) from 3.8 to 22.7% within a short period and are approaching commercialization. Such an outstanding advancement was realized by simply tuning the composition of the perovskite absorber layer. This compositional diversity allows tailoring of their photophysical properties, such as absorption coefficient, photoluminescence yield, and charge-carrier dynamics, which critically influence the PCE of a resulting device. In
this direction, we explored different sources of guanidinium cations to improve the photophysical properties, specifically, photoluminescence and charge-carrier dynamics of perovskite structures for their application in the fabrication of efficient solar cells. The effect of different sources of the guanidinium cations was systematically investigated by exploring various characterization techniques, including x-ray diffraction, scanning electron microscopy, steady-state absorption and emission spectroscopy, and time-resolved photoluminescence. The insights gained through these techniques helped us to understand the influence of guanidinium cations on the performance of PSCs. In my presentation, I will discuss structural, morphological and detailed photophysical characteristics of different perovskite films, and will correlate them with the photovoltaic performance of PSCs.

ES16.05.11 Ambient-Processed Perovskites for Broadband, Ultrafast and Efficient Flexible Photodetectors

Ivy Asuo1, 2, Paul Fourmont2, Ibrahim Ka2, Dawit M. Gedamu2, Soraya Bouzidi1, Alain Pignol1, Riad Nechache1 and Sylvain G. Cloutier1; 1INRS, Varennes, Quebec, Canada; 2Electrical Engineering, École de technologie supérieure (ETS), Montréal, Québec, Canada.

Organic-inorganic halide perovskites have shown exceptional semiconducting properties and microstructural versatility for inexpensive, solution-processable photovoltaic and other optoelectronic devices. The emerging solution-processed perovskite photodetector technologies show promising optoelectronic properties1–4 and generate a growing interest for large-area and flexible optoelectronic device production. In this work, we present a simple route for synthesizing efficient and reproducible halide perovskites under ambient conditions (>40%RH) by tailoring their physical and microstructural properties via mixed-anions and solvent additives. We fabricate an all-solution-based photodetector using high crystal quality perovskite nanowires grown on FTO and flexible Kapton substrates. The optimized photodetectors exhibit a high responsivity, a maximum specific detectivity of 10^12 cmHz^1/2/W and a rise time as low as 55 µs for devices on the rigid substrate and 320 µs for devices on the flexible substrate. It also shows remarkable photocurrent stability after multiple bending cycles. Moreover, due to the hygroscopic nature of halide perovskites, a deposition of poly(methyl methacrylate) (PMMA) as a protective layer on the perovskite yields significantly better stability under ambient air operation: the PMMA-protected devices are stable for over one month. This work demonstrates a cost-effective fabrication technique for high-performance flexible photodetector and will open opportunities for research advancements on broadband and large-scale flexible perovskite-based optoelectronic devices.


ES16.05.12 High-Efficiency Perovskite Solar Cell Fabricated by Slot-Die Coating Through Near-Infrared Heating in Ambient

Shih-Han Huang and Wei-Fang W. Su; Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan.

Low cost, solution processable perovskite solar cell has potential for large-scale fabrication. The slot-die coating is one of the solution process that uses less amount of material as compared with spin coating. Currently, the power conversion efficiency (PCE) of perovskite solar cell has reached to 18% by slot-die coating. However, the uniformity of perovskite film is determined by the rate of solvent evaporation that increase with gas quenching, vacuum quenching and thermal heating in the slot-die coating. In this work, we successfully fabricate the uniform perovskite film using near-infrared heating in 6 seconds. The highest PCE of 14.26% is reached for perovskite device without post annealing in ambient.

ES16.05.13 Thermionic Emission-Based Interconnecting Layer Featuring Solvent Resistance for Monolithic Tangent Solar Cells with Solution-Processed Perovskites

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Inorganic-organic perovskite is a promising material with unique high absorption coefficient, long carrier diffusion length, tunable bandgap, and simple preparation techniques for future photovoltaic development. The power conversion efficiency (PCE) of perovskite single-junction solar cells increases rapidly from 3.8% since 2009 to 22.7% in 2018. However, the PCE is ultimately limited by the Shockley-Queisser limit. All-perovskite tandem solar cell has been considered as the potential candidate for bring the PCE beyond the Shockley-Queisser limit of single-junction device and yet retaining the advantages of earth-abundant materials and solution processability. It is still a challenge to fabricate such solution-processed perovskite tandem device owing to the lack of robust interconnecting layers (ICL). The ICL should simultaneously achieve good electrical property for carrier transport and recombination, and high optical transmission. Meanwhile, the ICL should protect the bottom perovskite film against the damage of the solvent from the upper perovskite film because the solution process usually involves the same type of polar solvents. Here, a new thermionic emission-based ICL with enhanced solvent-resistance feature is demonstrated for monolithic tandem cells with solution-processed perovskite films. Fundamentally, the thermionic emission assisted solution-electron transport mechanism is confirmed through both experimental and theoretical studies. Meanwhile, the new ICL protects the underlying perovskite film from the solvents of the upper perovskite by introducing a fluoride silane-incorporated polyethylenimine ethoxylated (FSIP) hybrid system. Besides the solvent resistance function, this novel FSIP hybrid system passivates perovskite to reduce nonradiative recombination leading to considerable enhanced performance. With optimized ICL, the tandem cells demonstrate high PCE up to 17.9%, which is the highest among solution-processed all-perovskite tandem cells with indium free ICL. Consequently, this work contributes to not only understanding the fundamental mechanism of ICL but also to promoting robust and low-cost photovoltaics.

ES16.05.14 Diboron-Assisted Interfacial Defect Control Strategy for Highly Efficient Planar Perovskite Solar Cells

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Metal halide perovskite films are endowed with the nature of ions and polycrystalline.1 Formamidinium iodide (FAI)-based perovskite films, which include large cations (FA) incorporating into the crystal lattice, are most likely to induce local defects due to the presence of the unreacted FAI species.2,3 Here, we demonstrate a diboron assisted strategy to control the defects induced by the unreacted FAI both inside the grain boundaries and at the surface regions. The diboron compound (C₂H₃B₂O₃) can selectively react with unreacted FAI leading to reduced defect densities. Nonradiative recombination between a perovskite film and a hole-extraction layer was mitigated considerably after the introduction of the proposed approach and charge-carrier extraction was improved as well. We therefore obtained a champion power conversion efficiency of 21.11% with a stabilized power output of 20.83% at maximum power point for planar structure perovskite solar cells.4 The optimized device also delivered negligible hysteresis effect under various scanning conditions. This approach paves a new way for mitigating defects and improving device performance.

Reference:

ES16.05.15 Enhanced Performance of Perovskite Solar Cells by Micro-Structuring the Mesoporous TiO₂ Layer

Jingsong Sun1, 2, 3, Chang Liu2, 3, 4, Anthony Chesman3, 4 and Jacek Jasieniak2, 3, 4; 1Materials Science and Engineering, Monash University, Melbourne, Victoria, Australia; 2Monash Energy Materials and Systems Institute, Monash University, Melbourne, Victoria, Australia; 3ARC Centre of Excellence in Exciton Science, Melbourne, Victoria, Australia; 4Chemical Engineering, Monash University, Melbourne, Victoria, Australia.
Hybrid organic-inorganic halide perovskite solar cells (PSCs) have recently received tremendous attention and achieved high power conversion efficiency (PCE). However, efficient optimization of the PSC configuration is still key to further performance improvements. In this work, we report a facile method to develop high-efficiency PSCs by micro-structuring a mesoporous TiO$_2$ layer formed from directly from a TiO$_2$ nanoparticle dispersion. The micro-structuring is achieved through the controlled crystallization of additives in the dispersion, which are subsequently thermally fused following coating. This micro-structure enables for a more efficient charge extraction, achieving current densities of up to 24 mA cm$^{-2}$, some 5% higher than for pristine meso-porous TiO$_2$ layers. The PSCs using this modified TiO$_2$ mesoporous layer show the highest PCE of 19.6% compared to 18.6% for the controls. These results highlight that achieving high-performance PSCs relies not only on the nanoscale structure of charge extraction layers, but also their extended microstructure.

ES16.05.17  
Sustainable Pb$^0$ and Pb$^4$ Defects Elimination for Stable and Efficient Perovskite Solar Cells  
Lipeng Wang$^{1, 2}$, Ling-Dong Sun$^3$, Chun-Hua Yan$^1$ and Huaping Zhou$^2$; $^1$College of Chemistry and Molecular Engineering, Peking University, Beijing, China; $^2$College of Engineering, Peking University, Beijing, China.

Due to the soft nature of components in the metal halide perovskite absorber, it inevitably generates Pb$^+$ as not only recombination centers to deteriorate device efficiency, but also degradation starting point to hamper the device lifetime eventually. Herein, we demonstrate a sustainable Pb$^0$ and Pb$^4$ defects elimination method for the controls. These results highlight that achieving high-performance PSCs relies not only on the nanoscale structure of charge extraction layers, but also their extended microstructure.

ES16.05.18  
Analysis for Non-Radiative Recombination in Perovskite and Perovskite/Si Tandem Solar Cells  
Masafumi Yamaguchi, Ken-Hua Lee, Kenji Araki and Nobuaki Kojima; Toyota Technological Inst, Nagoya, Japan.

Remarkable recent advances in perovskite solar cells with efficiencies of over 23% have drawn world-wide as high-efficiency and low-cost solar cells. However, there are some problems to be solved in perovskite solar cells in order to develop high-efficiency, highly reliable and large-area solar cells and modules. Therefore, understanding and reducing non-radiative recombination losses in those materials and solar cells and resistance losses is necessary. In this paper, we introduced perovskite solar cells and perovskite/Si tandem solar cells is discussed by using external radiative efficiency (ERE), open-circuit voltage loss and fill factor loss and non-radiative recombination losses based on our previous analytical results for high-efficiency solar cells [1] and Si tandem solar cells [2]. One of problems to attain the higher efficiency perovskite solar cells is to reduce non-radiative recombination loss. The open-circuit voltage drop compared to bandgap energy (\(E_g\))/Vo(c) is expected to depend upon non-radiative voltage loss (Voc, rad) that is expressed by external radiative efficiency (ERE). Open-circuit voltage is expressed by

\[
V_{oc} = \frac{E_g}{1 + \frac{E_R}{E_g}}
\]

where the second term shows non-radiative voltage loss, and is radiative open-circuit voltage and 0.28V was used as the value for perovskite solar cells in this study. Correlation between Voc values for perovskite solar cells in the references estimated by eqs. (1) suggests that perovskite solar cells have still non-radiative loss and further improvements in efficiency are though to be possible by improving minority-carrier lifetime. In addition, reduction in resistance loss is suggested to be decreased. The perovskite solar cell have efficiency potential of 26% by improving ERE from around 0.3-1% to 20%. As one of non-radiative recombination loss issues in perovskite solar cells, effects of grain size upon minority-carrier diffusion length in perovskite solar cells are discussed. In order to improve ERE in perovskite solar cells, effects of photon recycling are also discussed. Recently, Si tandem solar cells including perovskite/Si tandem solar cells have become as one of hot topics. Most recently, 25.24% and 27.3% efficiency with perovskite/Si 2-junction tandem solar cells have been demonstrated by EPFL and Oxford Univ., respectively. Based on our analytical procedure [1,2], efficiency potential of perovskite/Si tandem solar cells is also analyzed in this paper. From the point of view of material quality, the ERE of perovskite/Si tandem solar cells are less than 10-5, which is several order-of-magnitude lower than that of III-V/Si tandem solar cells. This suggests that the material quality of perovskite/Si tandem cells still have large room to improve. By improving ERE from around 10 to 0.01, high efficiency of more than 33% is expected to be realized for perovskite/Si tandem solar cells. For this purpose, improvements in material quality, optimization of layer structures to reduce optical and resistance losses, and effective usage of light-trapping are suggested.

References  

ES16.05.19  
Side-Chain Polymer-Based Hole-Transporting Materials for High-Efficient Perovskite Solar Cells  
Yanyong Tian, Jianchang Wu, Chang Liu and Baomin Xu; Southern University of Science and Technology, Shenzhen, China.

In recent few years, the efficiency of organic-inorganic metal halide perovskite-based solar cells (PSCs) has been improved rapidly, because of the significant efforts in materials development and device fabrications. Hole transporting materials (HTMs) play an important role to the PSCs in charge extraction and interface modification. Currently, the most extensively studied and applied HTM for perovskite devices is 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD). However, the spiro-OMeTAD possesses relatively low intrinsic conductivities, which need dopants like lithium bis(trifluoromethanesulfonyl)-imide (Li-TFSI), cobalt complexes, or 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) to enhance the material conductivity. Thus, for simplifying the device fabrication, reducing the cost, and solving some trade-off between photovoltaic properties and long-term stability and to circumvent the tight control of doping level and oxidation duration in the fabrication procedure, numerous dopant-free HTMs including small molecules and conjugated polymers have been vigorously explored. Side-chain polymers play important roles in the polymer and materials science with abundance structures, flexibility, and moisture protection ability. However, only a few side-chain polymers like the poly(9-vinylcarbazole) (PVK) derivatives were studied in the PSC fields with moderate efficiency of around 16\%$^{[4, 5]}$. Herein, we designed new side-chain polymer structures by integrating a methoxytriphenylamine-conjugated-thiophene moiety as the HTM repeating unit on a poly styrene side-chain. The polymer (Poly-HTM) was synthesized by the radical polymerization of its relevant monomer (Mono-HTM). The results showed that with similar device preparation and measurement conditions, the hole mobility of polymer was about 3 times of that of its small molecular monomer. PSCs based on Poly-HTM as the dopant-free HTM afford an impressive highest power conversion efficiency of 17.2%, which is much higher than those obtained from Mono-HTM (9.7%). Moreover, the devices based on the Poly-HTM presented significantly higher stability than the device based on its monomer. Hence, this study demonstrates that the side-chain polymer strategy is an effective approach to achieve high efficiency and highly stable PSCs using dopant-free HTMs.

Reference  
ES16.05.20
Development Large Area Flexible Perovskite Solar Cells Using Embedded-Type Cu Mesh Transparent Conductive Electrodes Bu-Jong Kim1, Jincheol Kim2, Ekyu Han1, Jae-Sung Yun2 and Nochang Park1;1 Electronic Convergence Material & Device Research Center, Korea Electronics Technology Institute, Seong-Nam, Korea (the Republic of); 2Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington, New South Wales, Australia.

In recent years, research on organic-inorganic hybrid halide perovskite has been rapidly progressing due to its excellent photovoltaic materials having a large absorption coefficient, high carrier mobility, high carrier diffusion length, and direct band gap. Up to now, power conversion efficiencies (PCE) of perovskite solar cells (PSCs) have reached over 22%. The highest certified PCE of PSC has been achieved 22.7% on a small area. Despite a rapid increase in the performance, research for improving flexibility and large-scale PSCs that are advantageous in fabricating module and realizing commercialization are still insufficient. In order to fabricate flexible and large area PSCs, it is important to reduce the resistance and ensure flexibility of transparent conductive electrodes (TCEs). Meanwhile, Indium-tin oxide (ITO) or Fluorine doped tin oxide (FTO) thin films have been widely used due to their exceptional electrical properties, but we have disadvantages in the application for flexible devices, such as a brittle nature, a high processing temperature, and low adhesion to flexible substrate materials. For these reasons, studies on the electrode materials for replacing ITO and FTO, such as metal meshes, silver nanowires, conductive polymers, graphene, and carbon nanotubes, are actively progressing. Among these materials, metal meshes may be the leading candidates for commercialization due to their relatively low electric sheet resistance and high visible transmittance. However, a thick layer of metal mesh on the substrate, as required to achieve a sufficiently high conductivity in many applications, may easily cause electrical short circuiting. Furthermore, the flexibility of the embossed-type metal meshes was generally poor due to low adhesion between the flexible substrate and the metal mesh.

In this study, we present a fabrication method and properties of flexible and large area PSCs based on embedded-type Cu mesh. This is accomplished as follows: The Cu meshes are fabricated on glass substrates and then transferred to 5 cm x 5 cm Norland Optical Adhesive (NOA) as the flexible substrate. The opposite surface of NOA is patterned with a microstructure to improve the transmittance. Finally, the PSCs are deposited on embedded-type Cu mesh TCEs. The surface morphologies, cross section, and thickness profiles of the Cu mesh specimens are measured to confirm the thicknesses are well embedded in the NOA substrate, and their electrical and optical properties are characterized. Electroeluminescence (EL), quantum efficiency (QE), J-V, and Dark J-V are also measured for PSC fabricated on Cu mesh. Finally, the inner and outer bending tests are also performed to inspect the flexibility.

ES16.05.21
CHNH3PbI3 Exhibits Distinct NIR Sub-Gap Absorption Features in Response to AC Anodic and Cathodic Electrochemical Modulation Timothy Pollock and Cody Schlenker; University of Washington, Seattle, Washington, United States.

While lead halide-based perovskites have received an incredible amount of attention over the past several years as an emerging photovoltaic material, one aspect that has received minimal attention is their spectroelectrochemical responses in part to their relative instability under applied potentials while immersed in an electrolyte solution. We identify new spectrally distinct sub-gap NIR absorption features when we subject model CHNH3PbI3 perovskite solar cell materials to AC anodic and cathodic electrochemical potentials. First, we resolve a new differential absorption band with an onset near 850 nm under cathodic conditions, which is absent under anodic conditions. We find the electronic transition energy for this absorption to be commensurate with the energy separation that has been predicted and determined experimentally for the E1/2 and F1/2 conduction band minima in CH3NH3PbI3. Additionally, our AC spectroelectrochemical signals appear to be spectrally coincident with NIR transient absorption features that we observe on picosecond to nanosecond timescales. Deconvoluting these spectra by target analysis shows the correlation in temporal evolution between the photogenerated conduction band electron and trap state bleaching. The kinetics of the species associated spectra we model based on charge extraction, bimolecular recombination, charge trapping, and Auger recombination processes. The AC nature of our spectroelectrochemical detection also allows us to virtually eliminate the film degradation that has plagued DC electrochemical studies of halide perovskite materials. These results are relevant to device performance metrics as we see through kinetic modeling simulations that an extended electron lifetime observed in films made with 1-step fabrication procedure is due to a decreased trap state density compared to those made with a 2-step procedure, which also correlates to improved device performance due to increased fill factor.

ES16.05.22
Effects of Strain Modulation on the Charge Carrier Transport in 2D/3D Hybrid Formamidinium Perovskite Solar Cell Sungwon Song and Kilwon Cho; POSTECH, Pohang, Korea (the Republic of).

For commercialization of perovskite solar cell, suppression of ion migration and reduction of trap states is highly needed. Recent works has proposed that 2D perovskites with layered structures can be mixed with 3D perovskides due to its low defect density and superior ambient stability. Despite diversity of long organic cation, correlation of molecular structure and structural features and finally electrical properties have been neglected. Here, we systematically investigated the effect of the size of the phenylalkylammonium ions focusing on charge transport and defect passivation. The results show that defect density was reduced regardless of the type of phenylalkylammonium ion, however carrier accumulation and recombination loss in the perovskite crystals were increased with larger ion. Ionocation with steric hindrance induced tilting of lead-halide octahedra which affected charge collection efficiency. Finally, we could obtain highly efficient and stable (PCE=20.5%) low band gap (1.48eV) formamidinium perovskite solar cell.

ES16.05.23
High-Efficiency Perovskite Solar Cells Prepared by Low-Temperature Solution-Process for Commercialization Shih-Hsuan Chen, Ming-Chung Wu and Yen-Tung Lin; Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan.

With the shortage of energy, developing the alternative energy sources becomes an important issue. Solar energy is considered as one of the most important alternative energy source because it is inexhaustible. Among many types of solar cells, the metal halide perovskite solar cells (PSCs) is the most promising solar cells due to its high power conversion efficiency (PCE). The PCE of PSCs has rapidly increased from 3.8% to 23.3% since 2009. However, the high-efficiency PSCs typically required high-temperature-sintered mesoporous (over than 450°C) TiO2 (HT-TiO2) as electron transport layer (ETL) and the high-temperature to process often limits fabrication process. Furthermore, it can't be used on the flexible substrate and it will spend more energy on fabrication process. Based on above reasons, high-temperature to process is not suitable for commercialization. In this study, all the fabrication processes were under low temperature. The HT-TiO2 nanoparticles (LT-TiO2) were synthesized by non-hydrotalcite sol-gel method under 150°C and the spray-coating method was employed for the deposition of LT-TiO2 ETL. Moreover, we used spray-coating method and blade coating for large area (over 25 cm²) module. In order to go into commercialization, the perovskite active layer should be fabricated in the air. Therefore, we controlled different ratio of perovskite precursor solution (dimethyl sulphoxide:Butylacetone) to obtain large grain size, high crystalline, pinhole-free and uniform perovskite active layer with blade coating method under various relative humidity. We used scanning electron microscope and atomic force microscope to investigate the correlation between perovskite crystallization and various relative humidity. We also used the photo-assisted Kelvin probe force microscopy (KPFM) to explore the charge transport efficiency in active layer which were prepared under various relative humidity. Toward future commercial application, a large size module is essential. Hence, the 5x5 cm² PSCs module was fabricated based on the low-temperature process. Finally, we successfully developed PSCs without the need of high-temperature sintering process and obtained higher PCE than the mesoporous PSCs. The large area PSCs module also demonstrated the high PCE with the continuous process.

ES16.05.24
Ferroelectric, Photoconductivity and Photovoltaic Properties of Bi1−xCa2xF3−y/2O5/3u Thin Films Subhaist Nandy and Sudakar Chandran; Indian Institute of Technology Madras, Chennai, India.

The demand for renewable energy is escalating in recent years due to a dire need to address the global warming. Solar energy is one of the reliable alternative energy resources. Direct conversion of solar energy to electrical energy is a process known as photovoltaic conversion. Si based p-n junction solar cells with efficiency around 22% have captured commercial market despite high cost. Other solar cells based on semiconductor thin films, dye sensitizers, quantum dots, and organic inorganic perovskites are evolving to reduce the solar cell production cost while keeping up the efficiency similar to Si solar cells. Most of these devices are hampered by their long-term stability. In this front, all oxide photovoltaic devices are seems to be promising. Recently, ferroelectric oxides have captured significant attention in solar cell community due to demonstration of existence of unique anomalous photovoltaic effect, in which photovoltage (Voc) is found to be larger than the bandgap of the materials [1]. Most of the ferroelectric materials have larger bandgap – 3 eV which inhibits the material to absorb entire solar spectrum. Short circuit current density (Jsc) observed in ferroelectric oxide based solar cells is in the range of nA.
to μA which severely limits efficiency of the devices [2].

BiFeO₃ (BFO) is a room temperature ferroelectric oxide which exhibits lower bandgap ~ 2.5 eV in bulk. Bandgap of BFO can be tailored over a wide range from 2.32 eV to 1.5 eV [3], which is promising for solar cell application. In this report we show the effect of oxygen vacancies (Oᵥ) on ferroelectric, photoconductivity and photovoltaic properties of solar cells. The devices were made using BiₓCaₓFe₂₋ₓTiO₃⁺₀.₅ (BCFTO) [x = 0, (BFO); x = 0.1 and y = 0, (BC10FO); x = 0.2 and y = 0, (BC20FO); x = y = 0.1 (BC10FT100); x = y = 0.2 (BC20FT200)] thin films. All thin films are coated on FTO-glass substrates by simple spin coating. A mask having circular hole of 2 mm diameter is used to coat Au on top of the films. FTO/BCFTO/Au devices in capacitor configuration are used for photoconductivity and photovoltaic measurements. We observed an enhancement in photoconductivity of 3 orders in BC10FO and 5 orders in BC20FO compared to pristine BFO devices when illuminated with 1 Sun (~100 mW/cm²) power. Enhancement of photoconductivity in BC10FO and BC20FO is attributed to the Oᵥ present in the system. It is observed that Jsc is increased but Voc is reduced with increasing Ca doping concentration in pure BFO. FTO/BC20FO/Au and FTO/BC10FO/Au devices show Jsc = 3 mA/cm² and 30 μA/cm², respectively which are four and two orders larger than the Jsc observed in FTO/BFO/Au devices (~0.3 μA/cm²). Voc observed in pure BFO devices are ranging from 0.35 V to 3 V. In case of BC10FO devices, this lies in between 0.2 V to 0.8 V and it is found to decrease further for BC20FO devices (~0.1 V to 0.3 V). A reduction in ferroelectric domain size is observed with increasing Ca content. Ferroelectric switching gets diminished in BC10FO and BC20FO is attributed to the Oᵥ present in the system. It is observed that Jsc is increased but Voc is reduced with increasing Ca doping concentration in pure BFO.

In this work, we show our study on how the efficiency of the Perovskite solar cells depend on the conductivity and work function of PEDOT:PSS. A series of PEDOT:PSS solutions with different conductivity and work function were used to make the Perovskite solar cells. We will also report the interface processing we did in the p-i-n structure PSCs, which optimize device properties and charge transfer. In this work, all materials were prepared at low temperatures, showing potential for low-cost, scalable production of large-scale perovskite solar cells on flexible substrates.

References:

ES16.05.25 Perovskite Solar Cell—The Effect of PEDOT:PSS on Its Efficiency Hongkun Cai¹, Patrick Milan¹, Madison Guerrero¹, Jose Peralta¹ and Weining Wang¹, 1Seton Hall Univ, South Orange, New Jersey, United States; 2Electrical Science and Engineering, Nankai University, Tianjin, China.

The efficiency of Perovskite solar cells (PSC) has increased from 3% to 22% in less than eight years. Because of its rapid rise in efficiencies in recent cost fabrication process, the perovskite solar cell technology has been studied extensively and was named as one of the biggest scientific breakthroughs in the year of 2013 by Science. In the PSC structure, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is usually used as the hole transport layer (HTL) on top of ITO. It was found that interface engineering at electrodes is very important for increasing the performance of PSCs.

In this work, we study on how the efficiency of the Perovskite solar cells depend on the conductivity and work function of PEDOT:PSS. A series of PEDOT:PSS solutions with different conductivity and work function were used to make the Perovskite solar cells. We will also report the interface processing we did in the p-i-n structure PSCs, which optimize device properties and charge transfer. In this work, all materials were prepared at low temperatures, showing potential for low-cost, scalable production of large-scale perovskite solar cells on flexible substrates.

ES16.05.26 Study of Perovskite Thin Films Obtained by Conversion of Lead Iodide (PbI₂) Deposited by RF Sputtering Using Formamidinium and Methylammonium Solutions Nelson F. Villegas¹, José Maria C. Silva Filho¹, Rodrigo Szostak¹, Jean Carlos Da Silva², Ana F. Nogueira² and Francisco C. Marques², 1Gleb Wataghin Physics Institute, Unicamp, Campinas, Brazil; 2Chemistry Institute, Unicamp, Campinas, Brazil.

Perovskite materials have been used in the fabrication of solar cell with efficiency exceeding 22%. Some of the proposed perovskite structures uses solution process of lead iodide (PbI₂) as precursor. Here we propose the production of perovskite by using sputtered PbI₂. The films were deposited by sputtering a PbI₂ target prepared by compression of PbI powder and deposited at room temperature. The use of the sputtering technique allows the deposition of uniform films in large area. The films were converted in perovskite by using two routes: 1) spin coating the film with a solution of methylammonium iodide (MAI) and 2) dipping the film in the same solution. We also investigate the effect of using formamidinium iodide (FAI) and cesium iodide (CsI) solutions. X-ray measurements revealed that the PbI₂ films contain a small concentration of segregated lead (Pb) and that the perovskite films have (112) preferential orientation and some residual PbI₂. However, after conversion of the PbI₂ in perovskite we do not observe presence of segregated lead. Optical and structural properties were investigated through UV-Vis spectroscopy, SEM and AFM. Preliminary study of fabrication of perovskite solar cells supplied devices with efficiency of 2.5%. Optimization of the fabrication process is currently under way.

ES16.05.28 Effects of Environmental Factors on the Performance and Stability of Perovskite Solar Cells Iyotika Chakraborty and Lihong (Heidi) Jiao, Electrical Engineering, Grand Valley State University, Grand Rapids, Michigan, United States.

Perovskite solar cells (PSCs) are based on organo-metallic halides (perovskites) that act as a light-sensitive compound which produces excitons when placed under light. The general formula for a perovskite compound used in a PSC is expressed as ABX₃, where A is an organic/inorganic cation, B is a divalent metal cation and X are halide ions. The most common compound used in a PSC is methylammonium lead halide, CH₃NH₃PbI₃ (A = CH₃NH₃+, B = Pb²⁺; X = I⁻). The mesoporous TiO₂ layer. These materials possess optical and electronic properties that are required for high efficient photovoltaic devices. However, PSCs have a limited operating lifetime due to the degradation of the perovskite layer. There are many factors that lead to the degradation of the perovskite layer.

This study aims to investigate the environmental factors that affect the performance and long-term stability of the PSCs. The structure of the PSC is used in this study is the regular structure containing the TiO₂ perovskite absorber, hole transport layer and the carbon layer. The PSCs were fabricated using two different methods, the spin coating method. These solar cells were investigated under various environmental conditions like humidity (0 to 70%), with oxygen, without oxygen (nitrogen), normal environmental conditions, and longtime light soaking at elevated temperatures. The properties under investigations are the optical absorption of the perovskite absorber, the open circuit voltage (Voc), short circuit current (Isc), fill factor (FF), and efficiency of the PSCs. It was found that the PSCs do not degrade with the presence of oxygen in a dry and dark environment. The complete study of the effects of these environmental factors will be reported in this paper.

ES16.05.29 Investigating Viable Sn-Based Perovskite Solar Device by Utilizing a Cu₂O Hole Transport Layer (HTL), a Cu Back-Electrode and by In Situ Optimization of Component Layer Thickness Jalen Harris¹, Jon Shaffer², Michael Pham², Saqib Ahmed² and Sankha Banerjee¹, ¹Mechanical Engineering, California State University, Fresno, California, United States; ²Mechanical Engineering, Buffalo State College, Buffalo, California, United States.

This investigation has applied simulation work to elucidate the photovoltaic performance of non-Pb based perovskite devices, utilizing Sn. In an effort to address additional key criteria that impede the commercial realization of this technology, we have investigated Cu₂O (instead of the traditional spiro-OMeTAD) as an HTL that is cheap and easily synthesized, deposited and fabricated to form a fully functional device. Also, in an effort to reduce cost, in place of Ag as the back electrode, we have incorporated Cu. By optimizing each layer thickness, this work showcases not only a maximal efficiency device, but by critical analyses of Jsc, Voc and FF trends that manifest due to each component layer thickness modulation, we present key charge mobility and transfer kinetics within the structure of the cell. These optimal numbers and trends are critical when fabricating a physical device in the lab, and even more so once these components are investigated as viable ingredients in an industrial setting.

ES16.05.30 Simulation Studies on Optimizing Sn-Based Perovskite Solar Cell by Excluding Electron Transport Layer (ETL) and Modulating Device Component Thickness Jon Shaffer¹, Jalen Harris², Michael Pham³, Sankha Banerjee⁴ and Saqib Ahmed⁵, ¹Mechanical Engineering, Buffalo State College, Buffalo, New York, United States; ²Mechanical Engineering, California State University, Fresno, Fresno, California, United States; ³Mechanical Engineering, California State University, Fresno, Fresno, California, United States.

In this research, we have utilized simulation studies to probe non-toxic Sn-based perovskites with a goal to explore optimal fabrication methodologies. To that end, we have
investigated a device structure with and without an ETL and assessed the impact on critical photovoltaic parameters. Our ETL of choice has been the traditional TiO2 matrix, which has a wide bandgap, and good transport properties. We have also in-situ performed optimization of individual layer thicknesses, thereby ultimately fabricating a device with the highest possible theoretical efficiency. The analyses provide critical insight into charge mobility and charge transfer kinetics within this non-Pb based device; by observing the effects on Voc, FF, and FF as individual layer thicknesses are modulated, and doing comparisons of devices with and without an ETL, we present results of a structure that is not only optimal from an efficiency standpoint, but also from a technology viability and sustainability standpoint.

ES16.05.31
Planar Perovskite Solar Cells with SnO2; Electron Transporting Layer Deposited by Atomic Layer Deposition (ALD) Seonghwa Jeong, Seongrok Seo, Hyojeong Min Park and Hyunjung Shin; Department of energy science, Sungkyunkwan University, Suwon-si, Gyeonggi-do, Korea (the Republic of).

Recently, SnO2 has received a great deal of attention in normal perovskite solar cells with its excellent optical and electrical properties, wide bandgap, good chemical stability and can be grown by low temperature processing as an electron transporting layer (ETL). Among various deposition methods, SnO2 thin films used as ETL are deposited by Atomic Layer Deposition (ALD). ALD has the advantage of being able to control the film thickness with nanometer precision and to produce high quality thin film without any pinholes. Also, SnO2 has a a lower conduction band, compared to TiO2, which has energy level mismatch with MAPbI3, thus energetic alignment of SnO2 is more appropriate for extracting photogenerated electrons than TiO2. Thin films of Zn doped SnO2 also prepared in this study and showed enhanced conductivity compared to undoped ones, as a result, photovoltaic performances were improved in the normal planar structure (FTO / SnO2 / Perovskite / Spiro-OMeTAD / Ag) perovskite solar cells.

Keyword : perovskite solar cell, atomic layer deposition, zirconium doped SnOx

ES16.05.32
Optimization of Sb-Based Perovskite Solar Cell by Choosing Electron Transport Layer (ETL) and Modifying Device Component Thickness Michael Pham1, Jon Shaffer1, Jalen Harris2, Sanka Banerjee2 and Saqib Ahmed1; 1Mechanical Engineering, Buffalo State College, Buffalo, New York, United States; 2Mechanical Engineering, California State University, Fresno, Fresno, California, United States.

In this research, we have utilized simulation studies to probe non-toxic Sb-based perovskites with a goal to explore optimal fabrication methodologies. To that end, we have investigated a device structure with and without an ETL and assessed the impact on critical photovoltaic parameters. Our ETL of choice has been ZnO – which has a wide bandgap, and good transport properties. We have also in-situ performed optimization of individual layer thicknesses, thereby ultimately fabricating a device with the highest possible theoretical efficiency. The analyses provide critical insight into charge mobility and charge transfer kinetics within this non-Pb based device; by observing the effects on Voc, FF, and FF as individual layer thicknesses are modulated, and doing comparisons of devices with and without an ETL, we present results of a structure that is not only optimal from an efficiency standpoint, but also from a technology viability and sustainability standpoint.

ES16.05.33
Optically Controlled Two-Terminal Mechanical Perovskite/Silicon Tandem Solar Cells with Transparent Conductive Adhesives In Young Choi, Chan Ul Kim and Kyong Jin Choi; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Solar cell technology is evolving into solar cells that increase efficiency, reduce cost, or have special functions such as transparent or flexible solar cells. Silicon solar cell technology, which has a market share of more than 90% of the entire solar cell market, has a wide spectrum of BSF, PERC, HIT and IBC in terms of efficiency and price. However, it is difficult to meet the efficiency and price of silicon solar cell at the same time, and breakthrough technology is needed to overcome it. Among these breakthrough technologies, the most promising technique is a tandem cell strategy in which two or more solar cells with different band gap energies are stacked. In particular, perovskite solar cell is an ideal material for tandemization with silicon solar cells because it is easy to control the bandgap by adjusting the chemical composition of perovskite. Thanks to these advantages, perovskite/silicon tandem solar cells have been actively studied and some results with high efficiency above 20% already have been reported. However, Most of the reported perovskite/silicon tandem cell are based on the high-cost SI planar silicon solar cell due to the problem of uniform perovskite top layer. Here, we demonstrate a simple, low-cost, 2-terminal, silicon/perovskite mechanical tandem solar cell, which was fabricated by bonding a p-type silicon cell upside down on an n-i-p perovskite cell using a transparent conductive adhesive (TCA) layer. The TCA layer consists of Ag-coated poly(methyl 2-methacrylate) (PMMA) particles embedded in a polymer adhesive. The Ag-coated PMMA particles have the role of electrical current path and the polymer adhesive bond two sub-cells mechanically. The specific contact resistance and transmittance of the TCA layer was determined to be 5.46 x 104 ohm cm2 and > 97.0%, respectively. Because this TCA is flexible and soft, our tandem structure can use a conventional textured silicon solar cell compared to the other structures. Using optical simulations and experiments, the optimal current matching was achieved at a perovskite layer thickness of 150 nm for the CH3NH3PbI3 solar cell in n-i-p structure and Al BSF p-type Si cells. The tandem cell fabricated under the optimal current matching condition exhibited a current density of 15.43 mA/cm2, an open-circuit voltage of 1.59 V, and a fill factor of 79%, resulting in a steady-state PCE of 19.4%. To the best of our knowledge, the tandem cell efficiency of this study corresponds to the highest efficiency among all tandem cells based on Al-BSF silicon cells. The unique structure of this tandem cell showed excellent long term stability without encapsulation in a humid environment (100 h in RH 85%).

ES16.05.34
Effects of Urea Addition on Photovoltaic Properties of Perovskite Solar Cells Lingwei Li1, 2, Yuanqing Chen1, 2, Yang Song1, 2, Aditya S. Yerramilli1, Yuxia Shen1 and Terry Alford1, 2; 1SEMTE, Arizona State University, Tempe, Arizona, United States; 2Materials Physics and Chemistry, Xi'an University of Technology, Xi'an, China; 3Materials Science, African University of Science and Technology, Abuja, Nigeria.

The power conversion efficiency (PCE) of perovskite solar cells (PSC) continuously break new records; however, there are still big challenges for large perovskite fabrication. Two of these being the solar cell’s grain growth and stability. In this investigation, Urea additions to the perovskite precursor solution prepared using lead acetate precursors show improved device performance. The results show that the best content of Urea is 0.5 wt. %, when compared with the samples with and without Urea. The presence of Urea in the PSC increases the PCE of from 15% to 17%. X-ray diffraction analysis indicates that the addition of Urea promotes grain growth and also improves the grain’s orientation. This study reveals that the PCE is also closely related to the anneal time of the perovskite layer. Our findings show that the addition of Urea and proper anneal times enhance the crystallization process of the perovskite films and results in the resulting in larger and more orientated grains. This is the reason for the device’s improved carrier transport and conversion efficiency.

ES16.05.35
Long-Term Thermal and Operational Condition Stable Perovskite Solar Cells with Inorganic Charge Transport Layers Grown via Atomic Layer Deposition (ALD) Seongrok Seo, Seonghwa Jeong, Hyojeong Min Park, Nam-Gyu Park and Hyunjung Shin; Sungkyunkwan University, Suwon, Korea (the Republic of).

Despite the high power conversion efficiency (PCE) of perovskite solar cells (PSCs), poor long-term stability is one of the main obstacles preventing their commercialisation. Two of these being the solar cell’s grain growth and stability. In this investigation, Urea additions to the perovskite precursor solution prepared using lead acetate precursors show improved device performance. The results show that the best content of Urea is 0.5 wt. %, when compared with the samples with and without Urea. The presence of Urea in the PSC increases the PCE of from 15% to 17%. X-ray diffraction analysis indicates that the addition of Urea promotes grain growth and also improves the grain’s orientation. This study reveals that the PCE is also closely related to the anneal time of the perovskite layer. Our findings show that the addition of Urea and proper anneal times enhance the crystallization process of the perovskite films and results in the resulting in larger and more orientated grains. This is the reason for the device’s improved carrier transport and conversion efficiency.

ES16.05.36
Perovskite solar cells (PSCs) have attracted attention due to tremendous rise in the power conversion efficiencies (PCEs) over the past decade and their possibility to replace traditional silicon solar cells has become realistic [1]. Although high life time is key requirement, the research has been mainly focused on improving the efficiency. A few studies have been performed to improve the stability of PSCs by synthesizing new hole or electron transport layer [2]. In the inverted PSCs, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is the widely used hole transport layer (HTL), however, its acidic nature has been continuously raised as a concern for the long-term stability of PSCs. Therefore, there is an urgent need for other HTLs. Inorganic transport layers have been used in organic photovoltaics e.g. nickel oxide (NiOx), copper iodide (CuI), copper thiocyanate (CuSCN) which have found successful in improving the stability. These HTLs can potentially improve the stability of PSCs having an impact on bulk transport and interfacial charge collection properties.

In this study, we have tested six HTLs: PEDOT:PSS, NiOx, CuI, CuSCN, molybdenum oxide (MoOx) and vanadium pentoxide (V2O5) in the inverted perovskite solar cell structure. The used device structure was ITO/HTL/perovskite/Pc60BM:LiF/Ag, where FAxMxACryBBrxICy (M= Pb,Sn) (FMC) was the used as perovskite absorber layer. Stability tests were performed under continuous light exposure using an AM1.5G spectrum as well as using dark storage tests. Both the Power Conversion Efficiency (PCE) and lifetime were found dependent on the HTL material which was applied for the tests. PSCs with PEDOT:PSS showed the efficiency of 10.1 % which degraded to 60 % in 180 hours. PSCs with NiOx showed the highest efficiency (<12 %) and lifetime. NiOx based solar cell maintained the efficiency for more than 180 hours. Additionally, the PSC with NiOx also showed hysteresis free photovoltaic characteristics. CuSCN, MoOx and V2O5 based devices were also found to be more stable than PEDOT:PSS based device but with lower PCEs. To understand the degradation in more detail, slow-discharge mass spectroscopy was used to analyse the films before and after degradation. The results will be presented in this talk. Additionally, atomic force microscope and X-ray diffraction was used to support the results and compare between different HTLs. Morphology of perovskite was found to be extremely homogenous on inorganic HTLs supporting the solar cell performance which yielded the best performance. Overall, the results on inorganic perovskite is found to be the crucial factor affecting the stability of solar cell.

In conclusion, the inorganic transport layers shows improved stability for perovskite solar cells. NiOx was found to be the most efficient and stable hole transport layer.

References

ES16.05.37
High-Performing Perovskite Solar Cells Using Gallium Nitriles as Electron Transporting Layer by PEALD Xinhe Zheng, Huiyun Wei, Pen Qiu, Mingzeng Peng, Sanjie Liu, Yingfeng He, Yinneng Song and Yunlai An; University of Science and Technology Beijing, Beijing, China.

The self-limiting reactions of atomic layer deposition (ALD) enable conformal-coatings/ interface layers with molecular-level control of thickness and composition, which has been found great benefit in tuning the interfacial structure and properties in solar cells. So far, various metal oxides (TiOx, AlOx, ZrOx, SnOx, etc) deposited by ALD have been used in some new generation solar cells, however, few group-III nitriles (AlN, GaN, InN, etc) are reported to explore their application. Here, we study the application of GaN thin-films in perovskite solar cells (PSCs). The nitrides thin films are deposited via plasma enhanced atomic layer deposition (PEALD) by reaping the benefits of the lower deposition temperature and precise thickness control. The GaN thin film here serves electron transport layer (ETL) for PSCs. The results indicate that GaN thin-film thickness has a significant effect on the electron transport and collection of the photovoltaic cells. It is found that the devices based on the 50-cycle GaN thin-film (~5 nm) show the best cell efficiency with performance of 15.2%. The introduction of group-III nitrides has shown promise for improving solar cell performance, and further enhancement of cell efficiency via improving the nitrides quality.

ES16.05.38
Dopant-Free High-Performing Perovskite Solar Cells Using Gallium Nitriles and Grain Boundary Passivation in Highly Efficient and Stable Organic-Inorganic Hybrid Perovskite Solar Cells Aung Ko Ko Kyaw1, Fei Meng2, Xue Lai2, Xianqiang Li1, Wenhui Li1 and Gongqiang Li1; 1Southern University of Science and Technology, Shenzhen, China; 2Nanjing Tech University, Nanjing, China.

Hole transport layer (HTL), where photogenerated holes are extracted from perovskite and transported to the back-metal contact, plays an important role in enhancing the power conversion efficiency (PCE) as well as improving the stability, which is a major bottleneck for commercialization of perovskite solar cell (PSC). Currently, the state-of-the-art PSCs use the small molecule 2,2',7,7'-tetrakis[N,N-diphenylamino]-9,9'-spirobifluorene (Spiro-OMeTAD) or poly[bis(4-phenyl)(2,6-dimethylphenyl)amine](PTAA) doped with common additives, such as Li-TFSI and rib, which usually cause a serious degradation of device performance. Therefore, the development of dopant-free HTL becomes an essential requirement in the field of PSC. In this work, we designed and synthesized small-molecule-based dopant-free hole transporting material (HTM) called α, β-COTH-OMeTAD by fusing two strong electron donating moieties; saddle-shaped cyclooctatetrathiophene (COTh) and triphenylamine, to obtain sufficiently high hole transporting properties without additional dopants. The α, β-COTH-OMeTAD exhibits a deep highest occupied molecular orbital energy level (HOMO) of -5.3 eV and a high hole mobility of 2.88 × 10⁻⁶ cm²/V·s. The thermal decomposition temperature of this small molecule is 308 °C and the phase transition temperature is 121.5 °C, showing a good thermal stability. It also exhibits a good solubility in several common organic solvents, which is favourable for easy processability and device fabrication. The solar cell fabricated with our small molecule HTM in the structure of FTO/compact TiOx/perovskite/HTL/Au gives a PCE of 15.66% with Jsc = 21.05 mA cm⁻², Voc = 1.04 V and FF=71.79%, which is comparable to the device based on doped Spiro-OMeTAD as HTL, whose PCE is 16.96% (Jsc=20.24 mA cm⁻², Voc=1.10 V, FF=74.62%). In addition to functioning as HTM, α, β-COTH-OMeTAD also serves as an interfacial layer to passivate the grain boundaries of perovskite crystals. During the crystallization of perovskite film, solvent such as chlorobenzene (CB) or toluene is usually poured into the perovskite precursor solution under spinning to produce a uniform and high-quality perovskite film. Herein, we observed that incorporating a small amount of α, β-COTH-OMeTAD (10 mg/mL) in CB anti-solvent further improves the efficiency of solar cell. Using α, β-COTH-OMeTAD as both interfacial layer and HTL improves the PCE to 17.22% with Jsc = 21.51 mA cm⁻², Voc = 1.05 V and FF=76.37%. SEM image of perovskite film treated with α, β-COTH-OMeTAD exhibits less apparent grain boundaries and denser film because of the passivation effect. Time resolved photoluminescence (TRPL) measurement also reveals that the faster decay lifetime τ, which corresponds to the quenching of the photogenerated free carriers transporting from the perovskite to HTL becomes shorter but the slower decay lifetime τ, which represents the radiative recombination of free carriers becomes longer, suggesting the efficient charge transfer between the perovskite and HTL and good passivation effect of the α, β-COTH-OMeTAD. Besides the hole transporting and passivating properties, α, β-COTH-OMeTAD also improves the stability of the device due to the hydrophobic nature of the material which prevents moisture from penetrating into the perovskite film, and deep HOMO level which prevents from reaction with iodine in the perovskite compound. We also employed the commercially available conjugated polymer called PDHTBDT-FBT in a separate study. Different from α, β-COTH-OMeTAD, the PCE of device is very low when PDHTBDT-FBT is used as HTL but it is functioning well as interfacial layer to passivate the perovskite film. The PCE of 18.03% is obtained when PDHTBDT-FBT dissolved in CB is used as anti-solvent and spiro-OMeTAD as HTL.

ES16.05.39
Interfaces in Efficient and Stable Organic-Inorganic Hybrid Perovskite Solar Cells Ying-Chiao Wang, Takaaki Taniguchi and Kazuhiro Tsukagoshi; International Center for Young Scientists (ICYS) & International Centre for Materials Nanotechnologies (ICAMN), National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Since Prof. Miyasaka’s group first reported the organometal halide perovskite-sensitized photoelectrochemical cells in 2009,1 perovskite-based light harvesters have launched the photovoltaics revolution due to their key advantages of low cost and low processing temperature. Moreover, some superior material properties, such as the high absorption extinction coefficient in the visible-near infrared wavelength region and excellent photocarrier separation/transport characteristics,2,3 encourage the progressive development of organic-inorganic hybrid perovskite solar cells (PSCs).

After years of development, the power conversion efficiencies of PSCs have been dramatically increased to more than 20%, however, the instability issues are remain the obstacle to commercialization. In this seminar, I will discuss the relationship between interface engineering and the reliability of efficient PSCs. In addition, I will also introduce several strategies of designing the device interface and controlling the perovskite grain interface to achieve bendable and durable PSCs.

References
Although methyl ammonium lead halide (MAPbX$_3$) perovskites exhibit unprecedented photovoltaic potential with excellent optical and carrier transport properties; but the toxicity of lead and intrinsic instability are the main issue hampering commercialization of MAPbX$_3$ solar cells. Therefore, photovoltaic community giving great attention to bismuth halide perovskite material which has advantages of non-toxicity, ambient stability along with low-temperature solution-processability. Here, we prepared thin films of cesium bismuth iodide (Cs$_4$Bi$_2$I$_9$) materials using novel one-step spray coating method. Spray deposition technique is a versatile coating strategy that can be used to deposit thick layers of different materials over large areas at speed. An electric field generated by employing high DC voltage supply while spray deposition method. Applied voltages built-up the electric field to create negative ions. The resulting electric field helped to create charged nanoparticles that adhered to the substrate while depositing onto it. Thus, the ions and electrons got onto the substrate through the electric field. The ions then got converted into thick films of perovskite material.

Perovskite solar cells are especially promising when considering the technology lifespan. The advantages of using perovskite for the active layer include but are not limited to broad a light absorption spectrum, tunable band gaps, long charge carrier diffusion, and low fabrication cost. The current work involves the design, fabrication, and simulation of different configurations of Tin iodide active layer based lead-free perovskite solar cells. The goal of the project is to develop a configuration that is non-toxic as well as stable in natural open air environments with a specific resistance to moisture. This design incorporates the use of organic and inorganic materials, as well as the efficient use of the perovskite crystalline structure that is produced by using the properties of the active layer. Different economical hole transport layers has also been explored to evaluate the impacts on opto-electronics, and photon-to-current conversion efficiencies. The stacking structure is further modulated within the cell by progressively including a recombination-inhibiting thin TiO$_2$ or a ZnO layer with the FTO, followed by an electron-transport layer (various oxides) and a combination of CuOx/Cu as the hole transport layer and back contact electrode. This work is intended to build up to a broader project of selecting the most optimal low-toxicity perovskite cell to stack onto a Si or FTO bottom cell for tandem configurations.

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NH2O5 ETL layer to enhance the total stability of the solar cell. By controlling the oxygen vacancy of the NH2O5, we achieved the optimum efficiency of 16%. The vacuum-processed perovskite and carrier transport layer is thus very suitable for highly efficient and stable multi-junction solar cells.

ES16.05.46
Perovskite Solar Cells Using Low Temperature-Processed Nb:SnO2 Electron Transport Layer
Tae Hee Song, Kyoung Jin Choi, In Young Choi and Hyungmin Lee; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Recently, the development of solar cells using perovskite has been studied for past 10 years. In perovskite solar cells (PSCs), the electron transport layer (ETL) is an important component, which extract and convey electrons from perovskites to the cathode. This property has a direct influence on the efficiency of the cell. Since TiO2 has superior charge extraction and injection characteristics, most of high-efficiency PSCs use TiO2 and mesoporous TiO2 as ETL materials. However, TiO2 has several disadvantages such as vulnerable light stability against ultraviolet (UV) and low electron mobility which requires mesoporous TiO2 with high-temperature process (~450°C) so that there is limit of using in flexible substrates. As a result, studies on metal oxide as ETL that can be synthesized at low temperature and capable of planar structure have been actively researched. Among them, SnO2 has high mobility so that it enables fast transport of electrons and hysteresis-free can be obtained even in a planar structure. Also, SnO2 has a wide bandgap which leads stability against UV, and low photocurrent so that reduces current loss. For these reasons, SnO2 has been reported to be as efficient as a cell using TiO2. Moreover, since SnO2 is easily doped with various materials unlike TiO2, open circuit voltage (Voc) can be enhanced through bandgap alignment. Not only high efficiency, but also easy doping process could make SnO2 one of the most promising electron transport materials for planar perovskite solar cells.

In this work, we present a novel approach to engineer, and device design that has enabled these advances; and will review remaining challenges and paths forward for the field.

8:30 AM  *ES16.06.02*
Machine Learning to Tackle Perovskites’ Recovery and Degradation from the Macro- to the Nanoscale
Marina S. Leite; University of Maryland, College Park, Maryland, United States.

This talk will focus on the dynamic optical and electrical behavior of perovskites, from the macro- to the nanoscale. We investigate a series of hybrid perovskites, including MAPbI3, MAPbBr3, Cs2xFA1−xPb(IyBr1−y)3, and triple cation CsxFASnI3−xPbxBr1−yI3. To elucidate the contribution of humidity, oxygen, temperature, light, and bias on materials’ properties and devices’ performance, we combine advanced scanning probe methods based on photoluminescence (PL) microscopy and atomic force microscopy (AFM). Through environmental PL microscopy we identify a humidity-induced PL hysteresis that strongly depends on the Cs/Br ratio [1]. Using fast Kelvin-probe force microscopy we quantify a dynamic open-circuit voltage (Voc) response as a function of perovskite chemical composition and illumination treatment, as will be discussed in details during the presentation [2,3]. The individual and combined effects of each intrinsic and extrinsic parameter is analyzed in terms of a machine learning approach (ML), key to elucidate the device conditions that can prevent degradation, and enable rest and recovery. Our functional imaging platform [4–6], combined with ML [7], can be leveraged to identify the recovery conditions of emerging perovskities, including Pb-free options.

References:

9:00 AM  *ES16.06.03*
Next Generation Interface Modification Strategies for High-Performance Perovskite Optoelectronics
Nakita K. Noel; Princeton University, Princeton, New Jersey, United States.

Within the past few years, metal halide perovskites have been attracting significant interest due to their and their versatile use in a wide range of applications. These materials have been used in lasers, photodetectors, and most commonly, in photovoltaic devices and light emitting diodes. Despite the use and simple fabrication methods by which these materials are deposited, the resulting perovskite films are effectively high-quality semiconductors, and the power conversion efficiencies of lead halide perovskite solar cells are now exceeding certified values of 23%. However, perovskite-based devices are yet to achieve their full potential. One of the major hindrances to achieving this is an incomplete understanding of perovskite surfaces and interfaces. Deficiencies at these interfaces may be responsible for the largest losses in perovskite-based optoelectronic devices; limiting charge extraction, increasing non-radiative recombination rates and leading to hysteresis, and significantly increasing the voltage loss in perovskite photovoltaics. Herein, we will present interface modification strategies to mitigate these deficiencies. We utilise charge-transfer dopants to dope the perovskite at the interface, resulting in the formation of narrow homojunction. These homostructures result in reduced interfacial recombination, suppressed hysteresis and improved device performance, yielding steady-state device efficiencies of over 21%. We also explore the use fluoride-containing ionic liquids at the metal-oxide perovskite interface and show that not only do they affect the work function of the metal oxide, but also interact strongly with the perovskite, significantly improving the quality of the perovskite film. The utility of these interface modification strategies extends beyond perovskite solar cells and can also be used to further improve the performance of perovskite-based light-emitting diodes.

9:30 AM ES16.06.04
The Perovskite/Transport Layer Interfaces Dominate Non-Radiative Recombination in Efficient Perovskite Solar Cells
Martin Stolterfoht1, Pietro Caprioglio1, Christian Wolff1, Jose Marquez Puyol2, Ioleik Nordmann1, Shanshan Zhang1, Daniel Rothhardt1, Ulrich Hörmann2, Alex Redinger1, Lukas Keigelmann1, Steve Albrecht1, Thomas Kirchartz2, Michael Saliba2, Thomas Unold2 and Dieter Neher1; 1Institute of Physics and Astronomy, University of Potsdam, Potsdam-Golm, Germany; 2Department of Structure and Dynamics of Energy Materials, Helmholtz-Zentrum-Berlin, Berlin, Germany; 3Young Investigator Group Perovskite Tandem Solar Cells, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 4Institut für Energie- und Klimaforschung, Forschungszentrum Jülich GmbH, Jülich, Germany; 5Soft Matter Physics, Adolphe Merkle Institute, Fribourg, Switzerland.
Charge transport layers (CTLs) are key components of diffusion controlled perovskite solar cells, however, they can induce additional non-radiative recombination pathways which limit the open circuit voltage ($V_{OC}$) of the cell. In order to realize the full thermodynamic potential of the perovskite absorber, both the electron and hole transport layer (ETL-HTL) need to be as selective as possible. By measuring the quasi-Fermi level splitting (QFLS) of perovskite/CTL heterojunctions [1], we quantify the non-radiative interfacial recombination current for a wide range of commonly used CTLs, including various hole-transporting polymers, spiro-OMeTAD, metal oxides and fullerenes [2]. We find that all studied CTLs limit the $V_{OC}$ by inducing an additional non-radiative recombination current that is significantly larger than the loss in the neat perovskite and that the least-selective interface sets the upper limit for the $V_{OC}$ of the device. The results also show that the QFLS equals the internal QFLS in the absorber layer of pin and nip-type cells with selective CTLs and power conversion efficiencies of up to 21.4% (in pin). However, in case of less selective CTLs, the $V_{OC}$ is substantially lower than the QFLS which indicates additional losses at the contacts and/or interfaces. The findings are corroborated by rigorous device simulations which outline several important considerations to maximize the $V_{OC}$. This work shows that the real challenge to suppress non-radiative recombination losses in perovskite cells on their way to the radiative limit lies in the suppression of carrier recombination at the perovskite/CTL interfaces.

material electronic properties and stability. Furthermore, we determine the ideal Cl-incorporation ratio for stability increase without detrimental bandgap modification. The increased material stability induced by chlorine incorporation is verified by performing photoelectron spectroscopy on a device architecture. Our findings provide an important direction for the fabrication of stable perovskite devices.

References:

11:30 AM ES16.06.09
Structural and Theoretical Studies of Black Phases of CsPbI₂ — Influence of the Anharmonicity
Pedesseau Laurent1, Arthur Marronnier2, Guido Romani1, Soline Boyer- Richard3, Jean-Marc Jancu1, Yvan Bonnassieux2, Claudine Katn1, Costas Stoumpos2, Mercouri G. Kanatzidis3 and Jacky Even1; 1Univ Rennes, INSA Rennes, CNRS Institut FOTON - UMR 6802, Rennes, France; 2LPICM, CNRS, Ecole Polytechnique, Université Paris-Saclay, Palaiseau, France; 3DEN - Service de Recherches de Metallurgie Physique, CEA, Université Paris-Saclay, Gif sur Yvette, France; 4Univ Rennes, ENSCR, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, Rennes, France; 5Department of Chemistry and Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois, United States.

In less than 10 years, hybrid organic-inorganic perovskites have emerged as a new generation of absorber materials for high-efficiency and low-cost solar cells [1], [2]. More recently, fully inorganic perovskite quantum dots (QD) also led to promising efficiencies [3], [4] and then become a serious alternative to hybrid organic-inorganic perovskites. Currently, the record efficiency for QD solar cells is obtained with CsPbI₂. High resolution in-situ synchrotron XRD measurements have been performed on CsPbI₂ as a function of the temperature and revealed a highly anisotropic variation of the lattice parameters. Moreover, CsPbI₂ can be temporarily maintained in a perovskite-like structure down to room temperature, stabilizing a metastable perovskite polytype (black-phase) crucial for photovoltaic applications. Structural, vibrational and electronic properties of the three experimentally observed black phases are further scrutinized using theoretical approaches revealing the importance of the anharmonicity of the lattice [5], [6]. A symmetry-based tight-binding model, calibrated with self-consistent GW calculations including spin-orbit coupling, affords further insight into their electronic properties. A Rashba effect is thus predicted for both cubic and tetragonal phases when using the symmetry breaking structures obtained through frozen phonon calculations.

The ab initio simulations have been performed on HPC resources of CINES under the allocation 2017-J2017096724 made by GENCI (Grand Equipement National de Calcul Intensif).

11:45 AM ES16.06.10
Use of Meso-Structured PbI₂ for Two-Step Deposited Hybrid and All-Inorganic Perovskite Solar Cells
Bin Li1, Jianfeng Lu1, Jingsong Sun1, Liangchong Jiang1, Yi-bing Cheng1 and Jacky Jusienak2; 1Monash University, Clayton, Victoria, Australia; 2Wuhan University of Technology, Wuhan, China.

The so-called one-step and two-step sequential deposition methods are the most used in the fabrication of perovskite films suitable for deployment within solar cell structures. The one-step deposition approach relies on mixed metal and halide precursor solutions being processed under stringent conditions to control the extent of precipitation and, thus, to ensure high quality perovskite thin films. Whilst useful for small-scale devices, this approach is challenging to scale, which has prompted us to further explore the two-step method. In two-step sequential deposition, a high-quality perovskite film can be achieved by exposing a near lead halide film to a solution of an appropriate halide salt. In this work, we explore the role of solvent engineering to achieve microstructural control of the lead iodide (PbI₂) layer such that it is suitable for two-step sequential deposition. Through this modification, the diffusion of methylammonium iodide (MAI) into the structure to form methylammonium lead iodide perovskite during the second step is accelerated. Moreover, it enables for the formation of ultra-smooth thin perovskite films with large grains and photo-conversion efficiencies (PCE) of > 15% under planar configurations. The versatility of the approach is demonstrated also for all-inorganic CsPbBr₃Iₓ, with PCEs of > 10%.

1:30 PM ES16.07.01
Achieving Long-Term Thermal, Atmospheric and Operational Stability in Low Band Gap Tin-Lead Halide Perovskite Solar Cells
Rohit Prasanna1, 2, Tomas Leijtens2, Sean P. Dunfield2, James A. Raiford1, Eli Wolf2, 3, Giles Eperon1, Axel F. Palmstrom2, Maikel van Hest1, Stacey F. Bent1, Glenn Teeter1, Joseph Berry1 and Michael D. McGehee1; 1Stanford University, Stanford, California, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States; 3University of Colorado Boulder, Boulder, Colorado, United States.

Widespread adoption of renewable solar power requires the production of solar cells of improved power conversion efficiency at low cost. As conventional single-junction silicon solar cells approach their fundamental limits in efficiency, the use of tandem solar cells based on multiple semiconductors to absorb complementary parts of the solar spectrum offers a proven way to increase efficiency past 30%. Metal halide perovskite semiconductors, with their strong absorption, tunable band gaps, and defect tolerance under a variety of low-temperature processing methods offer the promise of fabricating such tandem solar cells at low cost. Specifically, all-perovskite tandems, which use perovskites for all active absorbers in the stack, promise to attain high efficiencies while keeping these benefits for all subcells. Over 20% efficient monolithic tandem solar cells have recently been demonstrated using a lead iodide-bromide perovskite for the wide-gap absorber and a tin-lead iodide perovskite for the low-gap absorber. While the use of tin at the B-site of the ABX₃ perovskite is crucial to achieving low band gaps required of the rear subcell, tin-containing perovskite solar cells have conventionally been thought to be unstable due to the propensity of tin to oxidize upon exposure to air. We show that tin can be drastically stabilized by alloying with lead, which leads the facile oxidation pathway that pure tin perovskites undergo. We identify two different reaction pathways by which tin-containing perovskites can be oxidized. The pathway that mixed tin-lead perovskites (with 50% tin or lower at the B-site) are forced to take involves breaking more Sn-I bonds, which makes it unfavorable, therefore stabilizing these perovskites toward oxidative breakdown.
We show that PEDOT:PSS, the hole transporter most commonly used so far for tin-containing perovskites, adversely reacts with them upon aging at elevated temperature (85°C). This results in poor thermal stability, with charge extraction being severely reduced upon 100 - 200 hours of aging at 85°C. By designing a heterojunction with upward band bending in the perovskite, we achieve selective extraction of holes without using the unstable PEDOT:PSS.

We proceed to study the effect of morphology on the rate of oxidation, and find that increasing compactness and size of nanoscale morphological domains significantly improves stability in air. Combining these results, we fabricate a mixed tin-lead perovskite using a hole-selective heterojunction, processed in a way that yields a compact and large-grained film, and show that this device maintains 95% of its initial efficiency after 1000 hours of aging at 85°C in ambient air without any additional encapsulation, and maintains 95% efficiency after 1000 hours of aging in damp heat (85°C with 85% relative humidity) with encapsulation. Further, the solar cell stays above its initial efficiency when operated at maximum power point under illumination for over 1000 hours. These results represent the first demonstration of the benchmark 1000-hour stability tests being passed by low band gap tin-lead perovskites. Our work removes the main perceived hurdle to the implementation of single junction and tandem solar cells based on tin-lead perovskites.


Perovskite solar cells (PSCs) have become a competitive photovoltaic (PV) technology with rapid progress of efficiencies reaching above 23%. Uniquely, PSCs have the highest efficiencies when they are solution processed, so one can envision solar cells printed in a similar manner and scale as newspapers. Bandgap tunability through perovskite composition engineering is attractive for developing high-efficiency multijunction devices, including perovskite/perovskite, perovskite/silicon, or perovskite/thin-film absorber (e.g., CIGS). In this talk, we will discuss our recent progress in the development of perovskite-based tandem solar cells. For wide-bandgap (~1.7–1.8 eV) PSCs, the challenge is to reduce the voltage deficit. Developing strategies to reduce defect density is critical. For low-bandgap (~1.2–1.3 eV) PSCs based on Sn-Pb mixed perovskite films, key challenges lie at both the material and device levels. At the material level, the high defect density associated with oxidation of Sn2+ to Sn4+ and formation of Sn vacancies significantly limits carrier lifetime and charge collection. At the device level, it is difficult to synthesize uniform, pinhole-free, Sn-based thin films because of the rapid crystallization of Sn-based perovskite films. We will show our recent progress on solution chemistry engineering to reduce defect density in perovskites with a wide composition range covering both low- and wide-bandgap perovskite films. The precursor chemistry and growth conditions affect significantly the physical and optoelectronic properties of perovskites. Finally, I will also discuss some of our recent efforts on upscaling PSCs. These results demonstrate a promising path towards commercialization of the perovskite photovoltaic technology.


Thin film tandem photovoltaic (PV) devices fabricated with commercially viable Cu(In,Ga)Se2 (CIGS) device as narrow bandgap bottom cell and emerging perovskite technology devices as wide bandgap devices for the top cell can offer low-cost and environmentally friendly solution processed route towards high efficiency devices. Another advantage in perovskite/CIGS tandems lies in variability of both top and bottom cell bandgaps. While multiple experimental and computational studies have optimized the perovskite/silicon tandem solar cells, the option of variability in the bottom cell material has been overlooked. In this study we have simulated performances of the perovskite/CIGS tandem solar cells in two-terminal and four-terminal configuration while varying both top and bottom cell bandgaps and perovskite layer thickness. To this end we use actual measured reflective indices for all the layers including the absorber layers within transfer matrix method calculations to determine the optimal bandgap combinations for the top and bottom cells. These devices are also examined for their energy yields in the context of real-world conditions. For this part of the study we generate annual hourly solar irradiance spectra using updated National Renewable Energy Laboratory’s typical meteorological year data while accounting for sunlight’s angles of incidence, PV device temperature and anisotropy in diffused horizontal irradiance for multiple locations in the USA. Our results show that certain combination of bandgaps for top and bottom cells do not perform as well under real-world conditions as they do for laboratory conditions. We explore the monthly spectral shifts due to seasonal climatic changes and demonstrate correspondence between the shifts in the solar irradiance spectra and functions of tandem devices.

2:30 PM BREAK

3:30 PM *ES16.07.04 Interfacial Design of Highly Efficient Vacuum-Deposited Perovskite Solar Cells Pablo Boix, Daniel Pérez-del-Rey, Chris Dressen, Ana Igual, Benedikt Dänekamp, Jorge Avila, Michele Sensollo and Henk J. Bolink; Instituto de Ciencia Molecular, University of Valencia, Paterna, Spain.

Vacuum-deposition of halide perovskites and charge-selective materials enables a wide range of variations in the device architecture [1]. This technique permits an accurate control on the layer thickness and stacking sequence, which is particularly suitable for applications such as tandem devices. Here, we use the intrinsically additive nature of vapor-based processes to carry out a detailed study of the solar cell interfaces and perovskite optoelectronic properties. We analyze the main processes determining the performance of both nip [2] and pin configurations [3]. The use of optical and electrochemical spectroscopies allows distinguishing the role of band alignment and recombination, and how these affect the open circuit voltage and overall performance of the devices. As a result, CH3NH3PbI3-based solar cells with open circuit potential close to the thermodynamical limit and power conversion efficiency >20% are achieved.

References

4:00 PM ES16.07.05 CdTe-Perovskite Tandem Photovoltaics Timothy Siegel, Tushar Shimpi, Walajabahad Sampath and Brian A. Korgel; McKetta Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, Texas, United States; Next Generation PV Center, Department of Mechanical Engineering, Colorado State University, Ft. Collins, Colorado, United States.

Hybrid organic-inorganic perovskites (HOIPs) have garnered significant interest as absorber layers in tandem photovoltaic devices (PVs) due to their low-temperature solution processability, high performance, and widely tunable band gap. Perovskites have been coupled in tandem devices with silicon, CIGS, and other perovskites, to boost the efficiency of the single-junction devices. However, they have yet to be employed in tandem with CdTe. One of the reasons for this is the need for a perovskite with either a very low or very high band gap to couple efficiently with the 1.5 eV band gap (Eg) of CdTe. Here, we show that tandem PVs can be made by coupling CdTe with wide band gap CH3NH3PbBr3 (MAPbBr3) in a four-terminal device architecture to improve efficiency. We find that MAPbBr3 films tend to exhibit a significant amount of haze, depending on the processing conditions of the film. This haze is a result of a “wrinkling” in the film, which is observed using polarized light microscopy and scanning electron microscopy. By simulating device performance with a MAPbBr3 top cell and a CdTe bottom cell using the Semiconductor Capacitance Simulator (SCAPS) software package, we identify the amount of haze that can be tolerated by the tandem device to still improve the performance relative to the CdTe device layer. We did this by applying optical filters to a simulated 15.5% power conversion efficiency (PCE) CdTe device and comparing simulated CdTe device PCE before and after the filter was applied. We see for a perfect MAPbBr3 top cell (100% transmittance E>2.3 eV, 0% transmittance E<2.3 eV), a MAPbBr3 device efficiency of 4.2% is required for the PCE of 4-terminal MAPbBr3-CdTe tandem to exceed 15.5%. Simulating instead a film with high haze, we show a MAPbBr3 top cell with 50% sub-band gap transmittance would require a PCE of at least 9.8% for break even. Finally, optimizing the MAPbBr3 top cell morphology, optical quality, and performance via solvent-antisolvent engineering and additive engineering, we construct and characterize HOIP-CdTe tandem devices.
Perovskite solar cells have shown tremendous improvement in their power conversion efficiency (PCE) in a short period of time reaching up to 23.3% [1]. Owing to excellent optical properties (sharp band-edge, high IR transmittance) and ability to tune their bandgap to wide energy range, make perovskites attractive candidates for top-cells in tandem applications [2].

We have previously demonstrated a 23.6% efficient monolithic, two-terminal perovskite/silicon tandem using 1.63 eV Cs$_{0.75}$FAPb$_{0.25}$Br$_3$ (CsFA) perovskite top-cell [3]. This PCE value is still below the 30% that is achievable with two junctions in two-terminal devices with silicon as a bottom sub-cell [2]. Reasons for low PCE include high reflectance loss due to planar front surface and parasitic absorption in layers other than perovskite and silicon. Additional way to improve PCE is to reduce the thermalization losses in tandem by using a perovskite top-cell of higher bandgap. Perovskite/silicon tandems are multi-layered devices, thus a comprehensive optical modeling is required to tune the thickness of perovskite top-cell to current-match it with silicon bottom-cell. To perform this analysis optical constants of wide-bandgap perovskites are required. So we first determined the optical constants using multi-angle spectroscopic ellipsometry and spectrophotometry of two CsFA perovskites having different bandgaps of 1.63 and 1.68 eV, and also of a common absorber, CH$_3$NH$_3$PbI$_3$. Then we showed that the complex refractive index of CH$_3$NH$_3$PbI$_3$, can be used to generate approximate optical constants for an arbitrary wide-bandgap perovskite (in the range of 1.56 eV to 1.68 eV) by translating the data along the wavelength axis. Lastly, we used these optical constants to map the short-circuit current density of perovskite/silicon tandems with a range of different bandgap perovskites and textures to determine the top-cell thicknesses necessary to achieve current matching for varying top-cell bandgap. Our results show that ~28% PCE tandem is achievable with 1.68 eV perovskite, and even higher efficiency is possible by minimizing parasitic losses.

In the end we fabricated a two-terminal perovskite/silicon tandem by employing a 1.68 eV Cs$_{0.75}$FAPb$_{0.25}$Br$_3$ (CsFA) perovskite top-cell, rear textured silicon bottom-cell and textured polydimethylsiloxane (PDMS) anti-reflection foil at the front achieving 25% PCE [4].


an impressive photovoltaic performance of 17.27% as compared to the standard spiro-OMeTAD-based device (18.01%). In addition, the SGT-421-based device exhibits improved long-term stability which is originated from the combination of various contributions such as larger water contact angle, good film-forming ability and trap passivation effect toward the perovskite films via Lewis acid-base interactions. Eventually, we believe in that the structure-property relationship study of the terminal acceptor units offer detailed understanding about their behaviour obtained from optical-electrochemical profiles with respect to the valence band of the perovskites. The apparent demonstration of multifunctional features together with high intrinsic hole mobility and excellent PCE by SGT-421 from the A-D-A-based HTMs shows that they can be a cost-effective and promising alternative to the expensive spiro-OMeTAD for PSCs applications. The facile synthesis of the HTMs from commercially available cheap starting materials opens up a new avenue for the commercialization of perovskite solar cells through the development of efficient and low-cost HTMs with multifunctional features.

ES16.08.02
An Investigation of Decomposition in Lead Halide Perovskites via In Situ Absorption Spectroscopy and Grazing Incidence Wide Angle X-Ray Scattering Soumya Kondu and Timothy Kelly; Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Moisture degradation is a serious hurdle for the commercialization of perovskite solar cells. Recently, mixed cation perovskites (MCPs) have shown promise in achieving relatively longer stability and consistently higher power conversion efficiency than single cation counterparts. Increased stability is due in part to the large grains created through the use of the mixed cation material, which leads to fewer pathways for the penetration of moisture. Furthermore, it has previously been shown that trapped charges are likely the core origin for degradation of perovskite material. Using MAPbI3/Br as control and CsFAMAPbI3/Br as the mixed cation perovskite, we measured trap density of states (tDoS) along the grain boundaries through KPFM and capacitance sweeps. These measurements were performed at 0%, 25%, 50%, and 75% relative humidity conditions for comparison. The mixed cation samples showed lower tDoS under moisture exposure, pointing to the reason for prolonged stability. Through this work, we can further understand the degradation pathway of mixed cation perovskite and the effect MA may play in the moisture stability of the device, moving one step closer to the commercialization of perovskite solar cells.

ES16.08.04
Carrier Cooling in Perovskite Under Hydrostatic Pressure Probed by Transient Absorption Spectroscopy Loreta A. Mascarella, Jan Versluis, Huib Bakker and Bruno Uhrer; FOM Institute AMOLF, Amsterdam, Netherlands.

The rise of the efficiency of perovskite solar cells from 3.8% to 23.3% in less than 10 years has shaken up the scientific photovoltaic community. A comprehensive understanding of fundamental properties of these intriguing materials is paramount for further progress in device applications. In this work we investigate how the charge carrier cooling dynamics in MAPbI3 thin films is affected by hydrostatic pressure up to 400MPa. In particular, charge cooling is probed by pump-probe transient absorption spectroscopy. We find a dramatic increase of carrier temperature at the picosecond timescale when the pressure is increased. We also investigate the effect of pressure on cooling timescales, as recently the slow cooling in those materials has sparked significant interest. Furthermore, we present a first insight on how the cooling is influenced by the phase transition, which occurs at around 325 MPa for this perovskite. Our findings will contribute to the understanding of ultrafast carrier dynamics of metal halide perovskites.

ES16.08.05
Perovskite Thin Films with Sub-Millimeter Grains Formed via Solvent Engineering Over Surface Modified Substrates Ricas Ahmad1,2, Tuck Ming Koh1, Nripsan Mathews1,3, Subodh Mhaisalkar1,3 and Maria-Elisabeth Michel-Beyerle4; Energy Research Institute @ NTU, Singapore, Singapore; 1-Interdisciplinary Graduate School, NTU Singapore, Singapore; 2-School of Materials Science and Engineering, NTU Singapore, Singapore; 3-School of Physical and Mathematical Sciences, NTU Singapore, Singapore, Singapore.

Improving the crystallinity is considered to be one of the most promising ways to enhance the efficiency as well as stability of lead halide perovskite photovoltaic (PV) devices. A typical high efficiency PV device employs perovskite thin films with grain sizes of the order of a few hundreds of nanometers. Even though there are reports showing the growth of perovskite monocrystalline thin films over substrates, these techniques cannot be scaled up to grow and fabricate devices beyond a few millimeters in lateral dimensions. Thin films with grain sizes of hundreds of microns is an attractive alternative to monocrystalline thin films as the device performance offered by such a film approaches monocrystalline device characteristics. Here we show that the substrate surface has a crucial role to play on the morphology and orientation of spin coated perovskite thin films. By tuning the substrate surface and engineering the precursor solution we were able to grow highly crystalline thin films of MAPbI3, and MAPbBr3, over different substrates. Typical lateral dimensions of individual crystal grains were found to be of the order of hundreds of microns (1000 times larger than conventional thin films) and were pin hole free. The thickness of these thin films were lesser than 1 microns and hence these films can be used to fabricate PV devices with excellent device stability and efficiency.

ES16.08.06
Superhydrophobic Perovskite Based on the Alkylamine Compound for High Efficiency Solar Cells Mi Hee Jung; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).

Hybrid quasi-two dimensional perovskites (2D) have attracted significant scientific interest because they have demonstrated excellent light absorbing materials in the photovoltaic devices. However, the quasi-2D perovskite still suffers in high humidity even though it exhibits greatly improved stability compared to their three-dimensional (3D) counterpart. This is the biggest obstacle to the realistic implementation of perovskite solar cells toward commercial viability. Herein, we used the hexylamine (CH3(CH2)6NH2) for quasi-2D, HA(CH3NH3)2PbI4 (n = 1, 2, 3 and 4) perovskites, has have enough long alkyl chain to maintain the chemical stability of perovskite. As the number of layers of quasi 2D HA(CH3NH3)2PbI4 perovskites was increased, it exhibited an appropriate band gap as a light absorber to be applied to solar cells. The perovskite solar cell based on the 2D HA(CH3NH3)2PbI4 perovskites shows superior power conversion efficiency of 11.5% with a 11.6% conversion efficiency of 23.4 mA cm-2, one open circuit voltage of 0.94 V and a fill factor of 71% as well as stability of solar cell to ambient air. The long alkyl chain of hexylamine cation prevent the degradation of the solar cell from the atmosphere by the passivation of perovskite films due to its highly hydrophobic property. This investigation highlights the role of organic cation to maintain the quality of perovskite film and provides a critical solution for the poor stability of perovskite in ambient air.

ES16.08.07
The Exploration of the Two-Dimensional Perovskites Incorporating Methylenammonium for the High Performance Solar Cell Mi Hee Jung; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).

In this study, we investigated the structural and optical properties of 2-dimensional (2D) perovskite according to the various cations, and synthesized mixed perovskites by incorporating them into the 3-dimensional (3D) perovskite (CH3NH3PbI3) in order to complement the disadvantages of the existing 3D perovskite. First, to prepare the 2D perovskites, we used the ammonium cations [butylammonium (BA), benzylammonium (BZA), ethylammonium (EA), guanidinium (GA), imidazolium (IM) and phenethylammonium (PEA)] as an organic component between inorganic layers based on a lead (II) iodide unit. When BZA, BA, and PEA were employed, we obtained
ES16.08.08
Enhancing Air Stability of Sn-based Metal Perovskite Materials by Chemical Doping
Myeongjung Lee1,2 and In Chung1,2
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Since the emergence of photovoltaic devices based on metal halide perovskite material, there has been extensive studies on replacing Pb for environmentally friendly technology. CsSnI3, a representative Pb-free halide perovskite material, suffers from critical problems. When exposed to air, it is immediately oxidized from Sn3+ to Sn4+, prompting rapid spontaneous phase transition from the perovskite (black phase) to the non-perovskite (yellow phase) structure. This air-instability prohibits its practical applications. Herein, we demonstrate a new strategy to improve the air stability of the black perovskite phase of CsSnI3, by chemical doping. We investigate structural changes of the undoped and doped black phase under various conditions, and find that moisture mainly causes the phase transition of the black phase. We reveal that specific dopants suppress the formation of competitive yellow phase by changing formation energy of Sn4+, and oxidation of Sn2+ in doped samples occurs at a significantly lower rate in air. As a result, doped CsSnI3, maintains the black phase over a week under air. These dopants induce an unusual shift in optical band gaps in Sn-based perovskite materials, in contrast to Pb-based materials. Ab initio density functional theory calculations show that band gap tuning effect is attributed to the p orbitals of the dopants.

ES16.08.09
High Performance and Long-Term Stability-Reduced Perovskite Solar Cells Based on Mesoscopic Zn-TiO2 Electron Transport Layer
Mine-Chung Wu, Shun-Hsiang Chan and Yi-Ying Li;
Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan City, Taiwan.

Organic-inorganic lead halide perovskite solar cells (PSCs) have attracted great interest due to its rapid progress in power conversion efficiency (PCE) within a few years, which is from 3.8% to the present record of 23.3%. However, this type of solar cell still exists some challenges to overcome. First, the toxicity issue of lead drags the PSC from commercialization. To advance the technology of PSC, the development of lead-free or lead-reduced perovskite is imperative. Second, the current density-voltage hysteresis (J-V hysteresis) is an important issue for PSCs. Especially, hysteresis effect often occurs in planar n-i-p structured PSCs. The hysteresis effect can lead to misjudgment of photovoltaic performance because the forward and reverse scans show different results. In order to solve these problems, we developed mesoscopic zinc-doped TiO2 (meso-Zn:TiO2) electron transport layer (ETL) and barium-doped perovskite (Ba-perovskite) active layer. The mesoscopic zinc-doped TiO2 (meso-Zn:TiO2) as ETL of PSC is synthesized by combining sol-gel and hydrothermal method. Surface morphology, electron mobility, charge carrier dynamic and electrical conductivity of various meso-Zn:TiO2 ETL are systematically studied. To understand the electron extraction behavior between perovskite active layer and meso-Zn:TiO2 ETL, the band levels and surface potentials of perovskite active layers are analyzed by ultraviolet photoelectron spectroscopy (UPS) and photo-assisted Kelvin probe force microscopy (KPFM), respectively. To achieve high PCE lead-reduced PSC, the stability of perovskite structure should be considered. By introducing formamidinium (FA) to Ba-perovskite, the crystallinity can be enhanced, which allows long-term stability for PSCs. The Ba-perovskite films are stable which can be fabricated in the atmosphere. In this study, we combined meso-Zn:TiO2 with Ba-perovskite to fabricate high-performance lead-reduced PSCs. By combining the benefits of both MAFA mixed-cation perovskite and Ba-perovskite, the acceptable doping amount of Ba2+ can be increased to >10.0 mol%, and the device performance is better than the MAPIPbI3 PSCs, indicating that mixed-cation perovskite is able to enhance the performance of lead-reduced perovskite and reduce the lead pollution to the environment. Obviously, when Ba-perovskite combines with meso-Zn:TiO2 ETL, the J-V hysteresis effect can be completely eliminated. These results show that the ETL-perovskite interface optimization could enhance PCE and eliminate J-V hysteresis.

ES16.08.10
Water Induced Defects Suppression for Efficient Inverted Perovskite Solar Cells
Ankur Solanki, Swee Sien Lim and Tze Chien Sum; Nanyang Technological University, Nanyang Link, Singapore.

Low power conversion efficiencies and material instability caused by moisture effects under ambient conditions are the pertinent issues for perovskite solar cells. Herein, an optimal small amount of water additive into methyl ammonium lead iodide (CH3NH3PbI3) solution helps to improve perovskite crystalization and stability of perovskite films. Addition of optimal fraction of water into N, N-dimethylformamide (DMF) results in controlled perovskite growth due to the higher vapour pressure and lower boiling point of water compared to DMF. The optimal water concentration of 1% by volume was found to yield preferential crystallization in the (110) plane, together with improved grain size, small amount of pin holes and defects compared to non-water added film. The device performance improved from 10.1% to 12.3% in 1% water added perovskite films, but decreases upon further inclusion of water content. Pump fluence dependent photoluminescence shows the reduced trap density from 4.8×1010/cm2 to 3.2×109/cm2 on inclusion of 1% water to the perovskite film. The presence of the optimal amount of water enhances the charge carrier lifetimes and diffusion lengths in blend film confirmed by the transient measurements and hence improved device performance. We conclude that these defects in perovskite are dominated by surface trap states and inclusion of an optimal amount of water as an additive help to passivate these traps. This study correlates the device performance, thin film morphology with transient dynamics and provide a route to control the growth of crystal perovskites and new insights for improving the stability of organic–inorganic halide perovskites.

ES16.08.11
Zirconium-Based Metal-Organic Framework as a Novel Interlayer Material for Efficient Perovskite Solar Cells
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Organic-inorganic hybrid halide perovskite solar cells (PeSCs) have risen as promising candidates for photovoltaics due to their superior properties such as outstanding performance, low cost and facile processability from solution state. In order to obtain higher power conversion efficiency of PeSCs, the suitable engineering of charge transport layers as well as the interlayer is needed. Herein, we first reported the application of a novel organic-inorganic based metal-organic frameworks (MOFs) as an interlayer for PeSCs which are porous coordination polymers exhibiting long-range ordered metal clusters connected with organic linkers. There are some reports expecting that MOFs could be utilized to optoelectronics, but a few reports regarding to MOF includes optoelectronics have also appeared. By using the rapid self-assembly process between metal source and organic linker to build MOFs structures, brushing method from precursor solution under hot-substrate condition was employed to prepare the thin MOFs films, incorporated into p-i-n structured PeSCs. By this straightforward strategy, the transparent and thin MOF films were deposited, film development and properties were analyzed by various methods and found to be appropriate for charge injection and transfer between perovskite and MOF layer. This result indicates MOFs could be novel and good hole transport materials for PeSCs.

ES16.08.12
Low Temperature Processed High Efficiency Flexible Perovskite Solar Cells with Additive-Induced Morphology Control
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Perovskite solar cells have been actively studied due to their great light absorption ability and a long excursion diffusion length (~ 1.0 μm). The cell efficiency has rapidly grown up to ~25% using mesoporous TiO2 layer which required a high temperature sintering processes. Such device structure with high temperature treatment is not compatible with flexible solar cells due to degradation of flexible substrate above 120°C. Therefore, low temperature process below the Tg of flexible substrate (PEN 120 °C, PET 80 °C) is necessary for the application to the flexible substrate. So we adopt planar type device structure of substrate/TiO2/polymer hole transport layer/amphiphilic conjugated
polyelectrolyte/MAPbI3(PCBM/BCP)/Ag with low temperature solution process (except BCP/Ag electrode). Also, we investigate the effect of various additives on crystal growth and grain size of perovskite films at different thermal annealing temperatures. The reasonably high efficiency of 18% and 17% fabricated at low temperature were obtained on glass and flexible substrates, respectively.

ES16.08.13

Eliminating Artifacts Resulted from Preferential Sputtering of Metal Halide Perovskite by Using Proper Sputter Source During ToF-SIMS Analysis Li-P. Jhong, Research Center for Applied Science, Academia Sinica, Taipei, Taiwan.

Recently, metal halide perovskite appears to be the most promising material in the photovoltaic devices. Despite the dramatic increase in the certified device efficiency, the lack of a comprehensive understanding of the fundamental properties, such as the real elemental composition and distribution in the perovskite film, greatly limits the technological progress. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful analytical tool which can provide one-dimension (depth profile), two-dimension (image mapping) and three-dimension (3D tomography) compositional information and it was used to probe the perovskite film or the entire perovskite solar cell. However, we found out that, during the sputtering period, the organic group locates at the A site in the perovskite lattice was removed at a much higher rate than the inorganic species when using the commonly utilized O2− sputter source. The unequal sputter rate of the components, which is also known as preferential sputtering, can misguide researchers to a false conclusion and stall the scientific advance. In this study, we demonstrated that by substituting C4H9+ for O2− as the sputter source, the preferential sputtering of organic species can be eliminated, yielding a depth profile without anomalous concentration gradient. We also investigated the 3D tomography of the perovskite film by using ToF-SIMS with C4H9+ sputtering. By comparing our results with those reported in the previous studies, the importance of using C4H9+ sputter source was highlighted for obtaining artifact-free information of metal halide perovskite via ToF-SIMS analysis.

ES16.08.14

Stability of Perovskite Photovoltaic Devices as a Function of Cation Composition Under Controlled Environmental Conditions Ramez Hosseinian Ahammadnejad, Zhaooning Song, Zahrah S. Almutawah, Adam Phillips, Yanfa Yan and Michael Heben; University of Toledo, Toledo, Ohio, United States.

Perovskite photovoltaic (PV) devices have demonstrated power conversion efficiencies above 23% within nearly a decade after their introduction. With such a remarkable rate of progress in performance and low manufacturing cost perovskite PV devices are expected to have a substantial share in the future PV industry. However, one of the major drawbacks of perovskite PV that hinders commercialization is lower stability compared to reliable and robust technologies such as Silicon and CdTe. While many methods such as employing multi-cation perovskite composition, mixed 3D-2D perovskite, and encapsulation have demonstrated enhanced lifetime for the perovskite PV devices, fabrication of durable perovskite solar cells remains a challenge. As a result, we introduced a new solution (named as solution B). Compared to the solution A, we used titanium isopropoxide (TiO2) as a metal source, which is a right choice to fabricate high stability perovskite solar cells. Finally, a highly reproducible fabrication procedure of PSCs with an average PCE of 16.5%, and a maximum PCE of 17.43% for an active area of 0.08 cm2 was achieved.

References:

ES16.08.15

Efficient Perovskite Solar Cells Using Atomic Layer Deposited Ti-Doped ZnO as a Transparent Contact Louise Ryan1, Arnaud Walter2, Matthias Bräuning2, Scott Monaghan1, Melissa M. McCarthy1, Shane O'Brien1, Mircea Medeoiu1, Martyn E. Pembble1,4, Sylvain Nicolay1 and Ian M. Povey1; Tyndall National Institute, Cork, Ireland; 1;Centre Suisse d’Electronique et de Microtechnique (CSEM), Neuchâtel, Switzerland; 2;École Polytechnique Fédérale de Lausanne (EPFL), Neuchâtel, Switzerland; 3;University College Cork, Cork, Ireland.

Power conversion efficiencies of perovskite (PK) solar cells have rapidly improved in recent years obtaining efficiencies in excess of 20% [1]. Good absorption properties in the visible and infrared spectrum, high efficiencies and low fabrication costs have brought PK solar cells to the forefront. With single junction PK solar cells soon reaching theoretical efficiency limits a requirement for tandem cells, where materials of differing absorption characteristics create a wider spectral range, is in demand. However, such tandem solar cells introduce fabrication complexities due to the thermal budget restrictions imposed by the complex layer structure [2].

Indium-tin oxide (ITO) is widely used as a transparent contact in PK cells. However, due to the high deposition temperatures or energetic process used in production ITO is not viable for tandem solar cells. Here we discuss the replacement of this transparent contact using atomic layer deposited (ALD) Ti-doped ZnO as a candidate material. ALD has the ability to be scaled and offers excellent uniformity even at low temperatures. We focus on the optimum deposition conditions of Ti-doped ZnO to optimize it and compare those to the commonly used ITO. Solar cells with Ti-doped ZnO transparent contacts were successfully fabricated and their performance, with respect to power conversion efficiency, evaluated and compared to state of the art PK solar cells.

References:

ES16.08.16

The Key Processing Issues and Their Solutions for High-Quality Perovskite Solar Cells Hojjatollah Sarvari, Mohsen Nasseri, So Min Park, Douglas Strachan, Kenneth R. Grahan, Vijay Singh and Zhi Chen; University of Kentucky, Lexington, Kentucky, United States.

Here, we report the critical processing issues and the solutions for the fabrication of cesium-doped mixed cation PSCs consisting of FTO/c-TiO2/mp-TiO2/Perovskite/spiro-OMeTAD/Au. Perovskite precursor with a final formula of C8H6[(MAPbBr3)x[(FAPbI3)y]1-x]0.5 is used. The perovskite film is deposited using the anti-solvent method through spin-coating and shows a smooth, shiny, and dark film. First, deposition of a pinhole-free c-TiO2 layer on a smooth surface is critical in the fabrication of high-efficiency planar perovskite solar cell structures. The conventional c-TiO2 solution for spin-coating a metal oxide is a mildly acidic solution of Diisopropanoxotitanium bis(acetylacetonate) (75% in 2-propanol) in ethanol named as solution A here. One needs to repeat the spin-coating of the c-TiO2 solution A two-three times to get rid of pinholes in the film. Thus, it uses extra effort, cost, time, and equipment into account, and the film will not be perfect. To tackle this issue, we introduced a new solution (named as solution B). Compared to the solution A, we used titanium isopropoxide (TiO2: 99.99%), hydrochloric acid, and anhydrous ethanol in solution B. We optimized this solution toward fabrication of a quick, pinhole-free, and efficient hole-blocking layer. Highly reproducible PSCs with an average power conversion efficiency (PCE) of 15.4% are fabricated using this solution compared to the conventional solution utilizing both spin-coating and spray pyrolysis with average PCEs of 10.6% and 13.78%, respectively.

The anti-solvent method was usually used with chlorobenzene (CBZ), but CBZ cannot dissolve the Li-TFSI particles which may be present on the surface of mp-TiO2 after Li-ion doping. In this case, we should use a solvent that can dissolve the Li-TFSI particles completely. Both diethyl ether (DEE) and the mixed solvent consists of CBZ and DEE with a volume ratio of 4:1 can dissolve the Li-TFSI powders easily. Perovskites with larger particles (from CBZ:DEE) show a lower density of defects in the film compared to the one with smaller particles. Thus, the performance of the PSCs with CBZ:DEE is improved. The overall PCE is enhanced to 15.9% for samples with CBZ:DEE compared to the PCE of 14.76% for samples with CBZ in the same processing conditions. Also, to improve the adhesion of Au to the HTL, a thin layer of silver (Ag) is introduced as the interlayer between the hole transport layer (HTL) and the Au. We deposited a 2-5 nm of Ag on top of the HTL followed by 80 nm of Au. In this way, the adhesion of the Au layer to the HTL is improved according to our simple tweezer tool test. A pure Au film can easily come off from the surface of HTL. However, the Au films with 2-5 nm silver buffer layer showed strong adhesion to the HTL. Interestingly, it improved the current density and, finally the PCE of the devices by both enhancing the adhesion of the back electrode onto the organic HTL and increasing the light reflection in the PSC.

Finally, a highly reproducible fabrication procedure of PSCs with an average PCE of 16.5%, and a maximum PCE of 17.43% for an active area of 0.08 cm2 in reverse bias direction is achieved.

ES16.08.17

Reducing Trap-Assisted Recombination in Pb-Less Perovskite Solar Cells by Combined Compositional and 2D/3D Engineering Deepak Thirumurahassery Gangadharan;
Halide perovskites have been dominating solution-processable photovoltaic research with remarkable power conversion efficiency of over 23%. The presence of toxic lead in state-of-the-art halide perovskite, however, shackles the marketability of this technology. Although by completely replacing lead with elements such as tin, germanium, etc. lead-free halide perovskite solar cells can be achieved, they show much lower efficiency and stability. Moreover, partially replacing lead with other metals helps to reduce the lead content in perovskite solar cells while without significant efficiency loss. But, we identify that trap-assisted recombination at grain boundaries and on the perovskite film surface associated with Sn vacancies limit the efficiency of three-dimensional (3D) Sn-Pb alloyed perovskite devices. By designing two-dimensional (2D/3D) alloyed perovskites, we passivated the non-radiative recombination channels and thus improved the efficiency of alloyed perovskite solar cells. Here, 2D/3D alloyed perovskites are synthesized by substituting small organic cations in 3D alloyed perovskoids with bulkier phenylhexylammonium cations. We optimized the content of lead and phenylhexylammonium cations for achieving the highest photovoltaic performance in resultant 2D/3D alloyed perovskite solar cells. Consequently, an enhancement of 39% was achieved in tin-rich alloyed perovskites (7.66 % versus 4.78 %) and a 15% enhancement in lead-rich alloyed perovskites (13.60 % versus 11.49 %) was achieved as compared to 3D alloyed perovskites in p-i-n planar solar cells. Also, the current-voltage hysteresis originating from the ion migration in perovskite almost fully vanishes in 2D/3D alloyed perovskite devices, once again attributed to the passivation of trap states, which is in clear contrast to the large hysteresis displayed in 3D alloyed perovskites. Last but not the least, 2D/3D alloyed perovskite devices showed much better moisture stability and photostability. The work demonstrates that a 2D/3D engineering strategy is an effective approach towards realizing Sn-based high-performance perovskite solar cells.

**ES16.08.18**
Rational Design of Low-Cost Hole Transport Materials for Highly Efficient Perovskite Solar Cells Yang Cao 1,1, Valerie A. Chiykowski 2 and Curtis Berlinguette 1,2; 1Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada; 2Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, British Columbia, Canada.

Expensive hole transport materials (HTMs) such as Spiro-OMeTAD and PTAA hinder the commercial deployment of high-efficiency perovskite solar cells (PSCs). We report an iterative approach to developing highly efficient HTMs from inexpensive organic scaffolds that give rise to high-efficiency PSCs without sophisticated device engineering. Candidate molecules with some structural variations were made within three synthetic steps. The structure-property relationship of these compounds was revealed by interrogating their physical (e.g., crystallinity and glass transition temperature) and electrical properties (e.g., work function and charge extraction from perovskite layer). This knowledge informs molecular modifications to achieve optimal parameters in thin-film devices. As the result, device PCE above 20% have been achieved in both direct and inverted device configurations.

**ES16.08.19**
Facile Synthesis of Composite Metal Nanostructures for High-Performance Planar Perovskite Solar Cells Chih Wei Chiu 1, Mriganka Singh 1 and Gang Li 2; 1Academia Sinica, Taiwan, Taiwan; 2Department of Electronic and Information Engineering,, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong.

Metal oxide carrier transporting layers have been investigated widely in organic/inorganic lead halide perovskite solar cells (PSCs). Tin oxide (SnO2) is a promising alternative to the titanium dioxide commonly used in the electron transporting layer (ETL), due to its tunable carrier concentration, high electron mobility, amenability to low-temperature annealing processing, and large band gap energy. In this study, a facile method was developed for the preparation of a room-temperature-processed SnO2 electron transporting material that provided a high-quality ETL, leading to PSCs displaying high power conversion efficiency (PCE) and stability. A novel physical ball milling method was first employed to prepare ground SnO2 nanoparticles (G-SnO2), and then a sol–gel process was used to prepare a compact SnO2 (C-SnO2) layer. The effects of various types of ETLs (C-SnO2, G-SnO2, G-SnO2/C-SnO2) on the performance of the PSCs are described. The composite SnO2 nanostructure formed a robust ETL having efficient carrier transport properties; accordingly, carrier recombination between the ETL and mixed perovskite was inhibited. PSCs incorporating C-SnO2, G-SnO2, and G-SnO2/C-SnO2 as ETLs provided PCEs of 16.60, 17.92, and 20.12%, respectively. In addition to their high efficiency, the devices featuring the composite SnO2 (G-SnO2/C-SnO2) nanostructures possessed excellent environmental stability—they maintained 99% (with encapsulation) and 93% (without encapsulation) of their initial PCEs after 105 days (~2500 h) and 60 days (~1400 h), respectively, when stored under dry ambient air (20 ± 5 RH %).

**ES16.08.20**
High Performance Planar Solar Cells Based on Quasi 2D Perovskite with Mixed Binary Organic Spacer Shi Chen and Baomin Xu; Southern University of Science and Technology, Shenzhen, China.

Ruddlesden-Popper layered quasi-two-dimensional (Q-2D) perovskites have shown promising stability, but the intrinsic insulating organic spacer layer mainly blocks the vertical charge transport and thus significantly depresses device power conversion efficiency (PCE). Moreover, most of the reported open-circuit voltage (VOC) values of Q-2D perovskite devices are still much smaller than 1.2 V. Herein, we design and fabricate a series of (PEA1-xBAx)2MAxPb3I13 (x ≤ 0.3, PEA = phenylhexylammonium, BA = n-butylammonium, MA = methylammonium) Q-2D perovskite films, and reveal that, compared to either BA or PEA unitary material, the mixed PEA-BA binary organic spacer leads to more intensified film surface quality, preferable vertical orientation of crystals and improved optoelectronic properties in respect to charge transfer dynamics, trap density and hole mobility. Consequently, (PEA0.75BA0.25)2MA0.3Pb1.7I3.3 based devices yield a maximum PCE of 14.1%, which is the highest efficiency for Q-2D perovskite (x ≤ 5, PEA or BA) devices so far. More importantly, a peak VOC of 1.21 V is achieved due to a small non-radiative recombination loss of ~100 mV, the lowest reported loss value for Q-2D perovskite devices. In addition, significant enhancement of PEA-BA based device performance parameters are also supported by obviously decreased recombination losses. These findings provide an effect strategy towards the rational design of Q-2D perovskite materials and device performance improvements.

**ES16.08.21**

Perovskite solar cell (PSC) has emerged as a promising photovoltaic technology in lab scale with a short time of research due to their high power conversion efficiency, simple device fabrication, all-solid-state structure and the possibility to integrate the traditional device into fiber format. The flexible electrode material is a key to develop the next perovskite solar cells devices. Therefore, we employed carbon nanotube yarn as working and counter electrode material in order to fabricate flexible perovskite solar cell. To achieve maximum photocurrent, we employ the most efficient and simple carbon nanotube yarn (CNT) synthesized using chemical vapor deposition to fabricate perovskite solar cell with carbon nanotube yarn as working and counter electrode. The electrical, optical and optoelectronic properties of the perovskite/carbon nanotube yarn device were measured and reported in this study.

**ES16.08.22**
Organic-Inorganic Bismuth (III)-Based Material—A Lead-Free, Air-Stable and Solution-Processable Light-Absorber Beyond Organolead Perovskites Miaoqiang Lyu; School of Chemical Engineering, Brisbane, Queensland, Australia.

Solar cells based on organolead halide perovskites have recently seen rapid progress as one of the most promising photovoltaic technologies, owing to their solution-processability, low-cost and high efficiencies [1-5]. However, serious concerns on the use of toxic lead as well as the instability of these perovskites in humid conditions have triggered efforts towards developing non-toxic and stable organic-inorganic alternatives, which is critically important for their market acceptance in future commercialization [6-8]. To address the toxicity and stability issue of the tin/lead based perovskites in this research field, we presented the first demonstration of applying organic-inorganic methylammonium bismuth (III) iodide (MBI) in solution-processable solar cells [10]. The organobismuth material shows the advantages of non-toxicity, ambient stability and low-temperature solution-processibility, which may provide promising solution to address the toxicity and stability challenges in perovskite solar cells. Systematic study have been performed to understand the electrical, optical and optoelectronic properties of the organic-inorganic methylammonium bismuth (III) iodide. Crystallographic data as well as the crystal structure of the MBI single-crystal was achieved using single-crystal X-ray diffraction. First-principles electronic band structure calculations based on the density
functional theory was carried out as well to determine the theoretical energy band structure and density of states in this semiconductor. According to the both the theoretical and experimental results, the energy band levels of the MBI are well-aligned to be used in a typical perovskite solar cells in replacing tin/lead perovskite layers. Therefore, solar cells based on the MBI films were assembled and tested. The devices yielded a preliminary efficiency of ~0.190% with an open-circuit voltage of ~ 0.510 V in its planar structure (Fig. 1 (a-c)). The MBI film shows good long-term stability in the ambient air, which has been confirmed by monitoring the time-dependent XRD results (Fig 1 (d)). Reducing the background carrier concentration and its optical band-gap may be two effective strategies for further improving the device performance. Also, this is one of the earliest demonstrations of trivalent metal cation based, solution-processable organic-inorganic hybrid light-absorber for solar cell application, which may inspire more research work to develop and apply organic-inorganic hybrid materials beyond divalent metal cations (Pb (II) and Sn (II)) for solar energy utility.

ES16.08.23
Can We Make Oxide Perovskite/Halide Perovskite Interfaces Selective? Anat Frizbak; Adi Karna2, Shay Tirosh2 and David Cahen1; 1Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel; 2Chemistry, Bar Ilan University, Ramat Gan, Israel.

Metal oxide perovskites (MOPs) are wide bandgap materials. Some MOPs are likely to have electron affinities (EAs) that make them suitable as Electron-selective Transport Layers (ETLs) in halide perovskite (HaP)-based solar cells. The rich substitution possibilities of oxide perovskites (regarding the A and B cations in these materials with ABO3 stoichiometry) allow tuning the EA to optimize them for use as ETL with HaPs. Sr- and Ba-based MOPs are particularly interesting as SrTiO3 has energy band positions similar to those of TiO2, the most commonly used ETL today. For BaTiO3 and BaSnO3, the EA is just 0.1 eV smaller and 0.3 eV larger than that of SrTiO3, respectively. We deposit MOPs solid solutions with a compositional spread by pulsed laser deposition as ETLs and measured the resulting distribution of lattice parameters and energy band positions. Onto this library, a uniform layer of mixed halide perovskite (HaP) absorber is deposited, and the effect of the different ETL compositions on the interface with the HaP absorber and transport across it is characterized. We will present results showing to which extent we achieve control over the interfacial energy band alignments. These data and conclusions then serve to find in how far the electronic energy level and structural measurements of separate layers can be used to optimize electron transport processes across the interfaces in complete solar cells (i.e., limits of vacuum level alignment).

ES16.08.24
An Upscaled Chemical Vapor Deposition Process (CVD) Claudiu Mortan; Energy Science and Engineering, Material Science and Surface Science Group, Technische Universität Darmstadt, Darmstadt, Germany.

An upscaled chemical vapor deposition process (CVD) for methylammonium lead iodide (MAPI, CH3NH3PbI3) and formamidinium lead iodide (FAPI, CH3NH2PbI3) used in thin film perovskite solar cells has been built-up and optimized. The procedure uses exclusively gaseous precursors to transform the inorganic salt, i.e. lead iodide (PbI2) to the respective perovskite films. The mechanism of formation has been confirmed using XPS and XRD. Further characterization techniques include SEM and solar simulator measurements.

SESSION ES16.09: Upscaling and Industrial Considerations
Session Chairs: Kylie Catchpole and Martin Stolterfoht
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 125 AB

8:00 AM *ES16.09.01
The Challenge of Pilot Scale Manufacturing Trials for Perovskite Solar Cell Modules via Sheet to Sheet and Roll to Roll Processing Trystan Watson, Jenny Baker, Daniel Barkitt, Simone Meroni, Katherine Hooper, Peter Greenwood, David Beynon, David Richards, Rahul Patidar, Dimitrios Raptis, Carys Worsley, Francesca De Rossi and Vassil Stoichkov; SPECIFIC, Swansea University, Swansea, United Kingdom.

Lead halide perovskite materials are particularly suited to solution processing and have been used extensively in coating processes combined with electron and hole transporting materials to produce multilayer solar cell devices with photovoltaic conversion efficiencies over 23%. The versatility of perovskite materials means that they can be applied to a range of substrates from glass to plastic and metal using a range of coating techniques from screen printing to spin and slot-die coating. This paper will consider the trials and tribulations of manufacturing perovskite solar cells at scale on glass and flexible PET substrates, in particular delivering an assessment on the matching of device architecture to deposition method to substrate with the view of unlocking scale-large production. The results will be discussed in the context of two recent pilot scale manufacturing trials on FTO coated glass and ITO coated PET.

In the first instance, the screen printing of glass mounted carbon perovskite solar cells (C-PSC), based on a triple mesoporous stack (titania, insulator, carbon) will be discussed. This structure represents likely the most promising architecture for successfully upsaling perovskite solar cells to modules and represents an exciting leap forward in the pursuit of industrial deployment with recent reports demonstrating 10,000 hours of continuous light soaking datausing inexpensive manufacturing processes. Alongside process improvements related to increasing throughput and mechanising manufacture, the performance and final cost of large area modules also depends on the ratio between the module’s active and total areas, the so-called geometrical fill factor, which has to be optimised to properly exploit the substrate available area and maximise the energy production. At present, series interconnected C-PSC modules are achieved through accurate registration of each of the patterned layers, using precision screen printing, however new developments will be presented using mechanical and laser scribing to increase the active area towards 90% for all printed modules.

Roll to roll processing of perovskite on PET requires a different approach primarily due to the temperature limitations of the substrate combined with the continuous non-batch deposition processes required. Here meniscus guide slot-die coating is used. Slot-die coating is a versatile technique able to coat a range of ink rheologies with little ink wastage. The paper will discuss the application of a meniscus guide to improving stripe definition, coating quality and reducing coating defects such as ribbing and discontinuous films. The lead iodide ink used in the perovskite layer is formulated in a non-toxic solvent and results in a film readily converted to perovskite through slot-die coating of methylammonium iodide without any other pre-treatments. The choice of solvent for the MAI ink is optimised by considering how the rheology and volatility of the formulation impacts on the conversion to perovskite. These developments allow us to demonstrate roll-to-roll coated perovskite solar cells.

Finally the paper will present the complex preparation required for the delivery of a pilot scale perovskite module trial. In order to transition from lab to module scale particular considerations for substrate and material handling are required. Extensive environmental monitoring was undertaken to understand and mitigate the potential for operator exposure and to ultimately ensure the safe delivery of these trials.

8:30 AM *ES16.09.02
Advances of Inverted Planar Heterojunction Perovskite Solar Cells Rui Zhu; Department of Physics, Peking University, Beijing, China.

Perovskite solar cells have attracted tremendous attentions in recent years due to the high device performance and the superior optoelectronic properties of perovskite materials. In this contribution, I will show our efforts on improving the device performance of inverted perovskite solar cells.[1-5] Research efforts, including the charge-carrier balance, composition optimization and in-situ dynamic observation of perovskite microstructure evolution, will be discussed.

REFERENCES
Organometal halide perovskites have powerful intrinsic potential to drive next generation solar technology, but their insufficient thermochanical reliability and unproven large-area manufacturability limit competition with incumbent silicon PV. The work addresses these limitations by leveraging large-area processing and robust inorganic hole transport layers (HTLs). We present inverted p-i-n perovskite solar cells utilizing NiO HTLs deposited by rapid aqueous spray-coating that outperform spin coated NiO and lead to a 5X improvement in the fracture energy ($G_c$), a primary metric of thermochanical stability. The morphology, chemical composition, and optoelectronic properties of the NiO films were characterized to understand and optimize compatibility with an archetype double cation perovskite, Cs$_2$FAPb$_{1-x}$Sn$_x$I$_{3}$)$_2$. Perovskite solar cells with sprayed NiO show higher photovoltaic performance, exhibiting up to 82% fill factor (FF) and 17.7% power conversion efficiency (PCE)—the highest PCE reported for inverted cells with scalable-processed charge transport layers—as well as excellent stability under full illumination and 4,000-hour aging. By utilizing open-air techniques and aqueous precursors, this combination of robust materials and low-cost processing provides a platform for scaling perovskite modules with long-term reliability.

9:15 AM

Mechanochemical Approaches to Inorganic-Hybrid Materials for Perovskite Solar Cells Daniel Prochowicz, Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland.

The discovery of hybrid organic-inorganic metal halide perovskites led to a renaissance of thin film photovoltaics. The great diversity of hybrid perovskite compositions and preparation paths makes them an excellent candidate for novel photovoltaic materials with unique combination of properties, the potential for low cost and easy processing along with relatively high power conversion efficiencies.\textsuperscript{2} Crystallinity, density of defects and impurities are key factors for optoelectronic properties, and are also highly dependent on the materials formation processes, for most inorganic semiconductors. Understanding this behaviour and the structure/property relationship is crucial for fundamental understanding of perovskite materials, and for extending their properties to other process-tolerant systems. In that context, the synthetic approach induced by mechanical forces has appeared as a new emerging methodology in materials science.\textsuperscript{3} The mechanochemical reactions in solid state offer a significant advance by avoid the use of solvent, dramatically shortening synthesis times and simultaneously increasing the purity and amount of product.

Herein, we present a facile mechanochemical route for the preparation of various hybrid perovskite particles for high-efficiency thin-film photovoltaics.\textsuperscript{5} We also demonstrate that such approach applied for preparation of perovskite materials has advantage over a solution-based synthetic routes in terms of hysteresis and device performance. In addition, mechanochemistry allows the facile synthesis of large quantities of polycrystalline materials that is particularly well-suited for solid-state NMR studies, which can provide direct information about cation dynamics and atomic level phase compositions.\textsuperscript{5} These studies highlight the essential need for atomic-level characterization of photovoltaic materials and provide fundamental understanding of photovoltaic parameters in these systems and their superior stability.

References


9:30 AM

High Photovoltaic for Inverted Planar Heterojunction Perovskite Solar Cells with Metal Oxide Hole and Electron Extraction Layers Xin Liu\textsuperscript{1} and Yanbo Li\textsuperscript{2}; \textsuperscript{1}Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Sichuan, China.

Organometal halide perovskite solar cells have been attracting increasing attention in recent years due to their excellent photovoltaic efficiencies, and that they possess the advantages of suitable optoelectronic attributes and simultaneously low-cost solution processibility. Recently, perovskite solar cells (PSCs) with inverted planar heterojunction structures, wherein a polycrystalline perovskite film is sandwiched between a hole and an electron-extraction layer, have gained attention due to its easy fabrication, compatibility with bending and greatly enhanced stability of energy-hand engine, and the possibility of fabricating multi-junction cells. Moreover, they have achieved power conversion efficiencies (PCE) exceeding 21%. Further improving their PCE is now mainly hindered by the relatively low open-circuit voltage ($V_{oc}$) and the relatively low short-circuit current density ($J_{sc}$) of perovskite solar cells.

In this work, we report an intense research on the optimization of the perovskite solar cells with NiO as hole extraction layer, in order to increase the open-circuit voltage ($V_{oc}$) and the short-circuit current density ($J_{sc}$). We found that the CsPbX$_2$ halides and favored by previous ball-milling of CsX and PbX$_2$ precursors. When bigger halides were used and/or CsX and PbX$_2$ precursors were simply mixed without previous post-deposition thermal annealing, as well as previous mechanosynthesis of perovskite powders. It is known that metal oxide demonstrate much higher carrier mobility and superior stability than organic materials. Here, we report a vacuum-deposition-based p-i-n type planar perovskite solar cell that uses metal oxide as hole and electron transport layers, respectively. This device structure shows a high $V_{oc}$ of 1.16 volts and 1.18 volts, corresponding to a voltage deficit of 0.45 volts at a bandgap of 1.61 electron volts and a voltage deficit of 0.47 volts at a bandgap of 1.65 electron volts, respectively, which derives from reducing nonradiative recombination.

9:45 AM

Single-Source Vacuum Deposition of Mechanosynthesized Inorganic Halide Perovskites Yousra El Ajjouri, Francisco Palazon, Michele Sessolo and Henk J. Bolink; \textsuperscript{1}University of Valencia Institute of Molecular Science, Valencia, Spain; \textsuperscript{2}University of Electronic Science and Technology of China, Sichuan, China.

Fully inorganic cesium lead halide perovskites are of great interest in the field of photovoltaics due to their optical and electronic properties and thermal stability.\textsuperscript{1–3} The poor solubility of Cs-based perovskites, which is encountered in conventional solution processing, can be bypassed by the use of vacuum deposition.\textsuperscript{4–6} This technique allows the formation of CsPbX$_2$ halide perovskite thin films in a dry process without the need of extra chemicals (e.g., solvents) other than the salt precursors that form the perovskite compounds. In this study, single-source vacuum deposition (SSVD) is used as an easy, fast and dry process for the preparation of fully inorganic cesium lead halide perovskite thin films.\textsuperscript{7} We investigated the structural and optical characteristics of the so-formed films as a function of chemical composition (chloride, bromide and iodide films were formed), post-deposition thermal annealing, as well as previous mechanosynthesis of perovskite powders. We found that the CsPbX$_2$ perovskite was preferentially formed for the smaller halides and favored by previous ball-milling of CsX and PbX$_2$ precursors. When bigger halides were used and/or CsX and PbX$_2$ precursors were simply mixed without previous mechanosynthesis, PbX$_2$-rich compounds such as CsPb$_2$X$_5$ were preferentially formed in the thin films. We demonstrate that single-source vacuum deposition of ball-milled perovskites represents an easy, fast and dry process to form high-quality thin films of fully inorganic perovskites. We will also present the preliminary implementation of these films into different optoelectronic devices such as light-emitting diodes or solar cells.


Perovskite photovoltaics has emerged as a new thriving technology for solar conversion due to the rapidly increasing power conversion efficiency (PCE). Although great progress has been made to push the PCEs of perovskite solar cells (PSCs) up to over 23% at laboratory scale, the practical conversion of solar energy to electricity via PSCs requires the development of large-area, low-cost, and stable high-efficiency PSCs. This presentation will introduce our recent efforts on the exploration of: 1) air blading as a new fully spin-coating-free and anti-solvent-free processing for scalable high-efficiency PSCs; 2) high-efficiency electron-transport-layer-free PSCs with simpler device configurations for low-cost and convenient device processing; 3) new low-cost and readily-available organic hole-transporting material for PSCs with efficiency over 20%; and 4) new insights into the stability of all-inorganic CsPbI3 photovoltaic. These results may contribute to develop practical perovskite photovoltaics.

References

11:00 AM ES16.09.08
**What’s the Story with Shockley and Queisser**

Chris Case, Oxford Photovoltaics, Oxford, United Kingdom.

Schokley and Queisser knew the absolute efficiency limit of single junction silicon long before technology caught up to within 90% of their 30% power conversion efficiency glass ceiling. The multijunction concept offers a roadmap for mass deployment of photovoltaic technology beyond 30%- raising the fundamental limit to 45% for silicon tandem and 40% for triple junction. In a few short years the perovskite technology has reached 23.3% in single junction and in tandem with silicon achieved 27.3% - exceeding for the first time the very best silicon single junction. Theoretical combination of existing best-in-class single junctions predict obtainable tandem and triple junction efficiencies of 34% and 39% respectively. So what is between us and the 34% efficient perovskite-silicon tandem? We discuss the specific challenges to overcome and our progress on the tandem roadmap beyond 30%, addressing fundamental loss mechanisms in the perovskite absorber and its contact heterojunctions as well as aspects of optical design and deployment in mono or bifacial format. We will address how these solutions can be delivered at the full wafer-scale in a production environment at rates of tens of thousands of wafers/hr.

11:15 AM ES16.09.09
**High Performance, Robust, and Stable Compound Perovskite Solar Cells with a Low-Cost Lens Array for Passive Tracking and Photon Management**

Oliver Zhao, Amprintz, Nicholas Rolston, Stephen Hamann, Reinhold D. Auskardt and Olav Solgaard; Stanford University, Stanford, California, United States.

Organic-inorganic metal halide perovskites have emerged as the most promising candidate for low-cost solar cells based on their compatibility with solution processing and rapid progress in device efficiency. Despite this remarkable potential, perovskites suffer from well-characterized chemical and thermal instability, as well as mechanical fragility; all of which are obstacles to achieve the required service lifetimes for commercialization. We previously introduced a new design concept of scaffold-reinforced compound solar cell (SCS), in which planar perovskite devices are partitioned into many smaller micrcells by a mechanically reinforcing scaffold. However, the introduction of scaffolds reduced device efficiency due to the parasitic absorption of the scaffold material, where the short-circuit current scaled inversely with the scaffold area (i.e., larger scaffolds resulted in lower current and efficiency).

In this work, we demonstrate a new low-cost lens array architecture which directs light away from the scaffold and into the perovskite micrcells, resulting in over 90% efficiency and current recovery. The microlens array is fabricated on the backside of the device substrate and uses light concentration to directly fabricate the scaffolds, thus making the scaffold self-aligned and removing the need for a photomask. In addition, both optical ray tracing simulations and light transmission experiments show that these lenses have passive light tracking capabilities up to angles of incidence greater than 30°, making them strong candidates for integration into low-cost, high-performance perovskite devices. Finally, we demonstrate the thermomechanical reliability of these lenses under accelerated aging conditions which is imperative for longer service lifetimes so that perovskite solar cells can ultimately compete with CIGS, CdTe, and e-Si solar technology.

11:30 AM ES16.09.10
**Perovskite Ink Chemistry—A Key for Scalable Anti-Solvent-Free Deposition Technique**

Benny Febriansyah, Teck Ming Koh, Nripun Mathews and Subodh Mhaisalkar; Energy Research Institute @NTU, Singapore, Singapore.

Lately, tremendous effort has been made, particularly in laboratory-scale spin-coating technique, to achieve unprecedented increase in power conversion efficiencies of perovskite solar cells (23.7%). However, the reported efficiency are mainly based on small-area perovskite solar cells (≤0.1 cm²). Scalable processing methods are still lagging behind the state-of-the-art spin-coated devices, primarily due to the complexity in perovskite casting, drying and crystallization from its precursor solution. It can be foreseen that the upcoming challenge for commercializing perovskite PV technology will be translation of high quality perovskite film from laboratory-scale spin coating technique to large-area coating or printing methods. Since the perovskite ink chemistry for scalable deposition was underexplored, we demonstrated new perovskite ink formulation for single step anti-solvent-free deposition for high efficiency perovskite solar cells and its potential of fabricating large-area devices.

SESSION ES16.10: Beyond Solar Cells and New Materials

**Session Chairs:** Anita Ho-Baillie and Yixin Zhao

Thursday Afternoon, April 25, 2019

PCC North, 100 Level, Room 125 AB

1:30 PM ES16.10.01
**Photoluminescence Mechanisms in MAPbBr3 Films with Controlled Crystal Size**

Nikolaos Droseros 1,2, Giulia Longo 1, Jan Brauer 2, Michele Sessolo 1, Henk J. Bolink 1 and Natalie Banerji 1; 1 Dept. of Chemistry and Biochemistry, University of Bern, Bern, Switzerland; 2University of Fribourg, Bern, Switzerland; 3Instituto de Ciencia Molecular, University of Valencia, Paterna, Spain.
Organo-lead halide perovskites are excellent candidates for applications in light emitting diodes (LEDs). Methylammonium lead bromide (MAPbBr₃) is the most investigated perovskite for visible perovskite LEDs, but its use is still limited by a low photoluminescence quantum yield (PLQY). Efforts to increase the PLQY of this material mainly consist in fine-tuning the morphology and reducing the grain size of the polycrystalline perovskite to the micro- and nanoscale. However, the origins of the increased PLQY with reduced crystal size remain unclear. Here we elucidate the physical processes underlying the light emission of MAPbBr₃ thin films using time-resolved spectroscopy. A systematic correlation between the enhanced PL properties and the reduction of the crystal size, achieved by using different additives during solution-processing, is observed. The co-existence of free carriers and excitons at low excitation densities is shown in as-cast polycrystalline MAPbBr₃ (crystal size of the order of few μm), while only excitons are present at high excitation densities. Using the Burstein-Moss and Saha models, important quantities such as the exciton binding energy, the reduced exciton effective mass and the trap density are estimated. We then explain the increased PLQY upon crystal size reduction by the presence of a bright exclusively excitonic population even at low excitation densities, together with reduced surface trapping thanks to passivation by the additives. J. N. Droseros, G. Longo, J. C. Brauer, M. Sessoło, H. J. Bolink, N. Banerji. ACS Energy Lett. (2018), 3, 1458

1:45 PM ES16.10.02
Simulation Studies of Useable Perovskite Photovoltaic Devices—Non-Toxic, Cheap Material Alternatives That Have Been Optimized In Situ with Their Thicknesses Jalen Harris¹, Jon Shaffer², Michael Phant³, Sanhita Banerjee¹ and Sajib Ahmed²; Mechanical Engineering, California State University, Fresno, Fresno, California, United States; ²Mechanical Engineering, Buffalo State College, BUFFALO, New York, United States.

In this research, we have utilized simulation studies to probe non-toxic Sn and Pb-based perovskites with a goal to explore optimal fabrication methodologies. To that end, we have investigated a device structure with and without an ETL (both TiO₂ and ZnO have been explored) and assessed the impact on critical photovoltaic parameters. We have also explored Cu₂O as a viable hole transport layer (HTL) alternative to the traditional Spiro OMeTAD structure owing to ease of fabrication. Lastly, we have incorporated Cu as a viable back-contact alternative to the expensive Ag. We have performed optimization of individual layer thicknesses, thereby ultimately fabricating a device with the highest possible theoretical efficiency. The analyses provide critical insight into charge mobility and charge transfer kinetics within this non-Pb based device with cheap and easily fabricated materials. By observing the effects on Jsc, Voc, and FF as individual layer thicknesses are modulated, and doing comparisons of structures with and without the various ETL layers, we present results of a structure that is not only optimal from an efficiency standpoint, but also from a technology viability and sustainability standpoint.

2:00 PM *ES16.10.03
Encapsulating Perovskite Solar Cells to Withstand Environmental Stress Anita Ho-Baillie; Australian Centre for Advanced Photovoltaics, University of New South Wales, Sydney, New South Wales, Australia.

While energy conversion efficiencies of metal halide perovskite solar cells continue to improve (from 3.8 % to 23.7 % in merely 9 years), durability becomes an even more pressing issue especially for practical applications. In particular, solar cells need to endure environmental stresses such as moisture, heat and light. I will talk about some of the simple encapsulation schemes developed in my research group for moisture and heat stabilities. It is found that high quality barrier film when applied appropriately is sufficient for perovskite solar cells to pass IEC61215:201615 thermal cycling, damp heat and humidity freeze tests. The pressing pressure when applying barrier-film-based encapsulation and the design of the cell solar structures play a key role in module durability. Preliminary results of gas chromatography and mass spectrometry will also be presented to investigate trends of outgassing by perovskite solar cells which are useful information for designing appropriate encapsulation schemes.

2:30 PM ES16.10.04
Ionotronic Halide Perovskite Diffusive Synapses for Low-Power Neuromorphic Computation Rohit A. John¹, Natalia Yantara², Filippo De Angelis²,³, Subodh Mhaisalkar¹, Arindam Banu¹ and Nirpan Mathews³; ¹Nanyang Technological University, Singapore, Singapore; ²Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore; ³Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Perugia, Italy; ⁴D3-Computation, Istituto Italiano di Tecnologia, Genova, Italy.

Emulation of brain-like signal processing is the foundation for development of efficient learning circuitry, but few devices offer the tunable conductance range necessary for mimicking spatiotemporal plasticity in biological synapses. An ionic semiconductor which couples electronic transitions with drift-diffusive ionic kinetics would enable energy-efficient analog-like switching of metastable conductance-states. Here, we utilize ionic-electronic coupling in halide perovskite semiconductors to create memristive synapses with a dynamic continuous transition of conductance-states. Co-existence of carrier injection barriers and ion migration in the perovskite films defines the degree of synaptic plasticity, more notable for the larger ionic ammonium and ammonium cations than the inorganic cesium counterpart. Optimized pulsing schemes facilitates a balanced interplay of short and long-term plasticity rules like paired-pulse facilitation and spike-time dependent plasticity, cardinal for learning and computing. Trained as a memory array, halide perovskite synapses demonstrate reconfigurability, learning, forgetting and fault tolerance analogous to the human brain. Network-level simulations of unsupervised learning of handwritten digit images utilizing experimentally derived device parameters, validates the utility of these memristors for energy-efficient neuromorphic computation, paving way for novel ionotronic neuromorphic architectures with halide perovskites as the active material.

2:45 PM ES16.10.05
Dual-Source Evaporation of Multidimensional Semiconductor Bismuth Halides for Planar Junction Solar Cells Maryam Khazaee contempt; Kasia Sanders²; Chang-Chang Chung¹, Jon-Paul Sun¹, Hanchun Zhou¹, Charlotte Clegg³, Eric Bergmann⁴, Wiley A. Dunlap-Shohl⁵, Qiwu Han⁶, Ian G. Hill⁷, Jacob L. Jones⁸, Dora C. Lupascu⁶ and David B. Mitzi⁸,¹; ¹Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States; ²Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), Essen, Germany; ³Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; ⁴Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada; ⁵Department of Chemistry, Duke University, Durham, North Carolina, United States.

Despite the significant progress in fabricating hybrid organic-inorganic lead halide perovskite solar cells, their toxicity and low stability remain as major drawbacks, thereby hindering large-scale commercialization. Given the ionic/electronic nature of lead(II) and bismuth(III) ions, potentially stable and non-toxic alternatives for efficient light absorption in thin-film photovoltaic (PV) devices may be found among bismuth-based halide semiconductors. Recently, solution-based film fabrication approaches for several bismuth-based iodide semiconductors have been investigated. The current work reports on a facile and reproducible two-step coevaporation/annealing approach to fabricate AgBiI₃ (A = Cs, Rb, Ag₂BiI₇, Ag₃BiI₈ and Ag₅BiI₁₁) polycrystalline films with compact and pinhole-free morphology (Chem Mater., 2018, 30, 3338-3354). The structural, compositional, optical and electrical characteristics of the resulting thin films are studied by X-ray diffraction, scanning electron microscopy (SEM) energy-dispersive X-ray spectroscopy (EDX), optical spectroscopy and X-ray/UV photoelectron spectroscopy. A crystalllographic phase transition from rhombohedral to cubic structure silver bismuth iodide is investigated via temperature-dependent X-ray diffraction (TXRD). Planar-junction photovoltaic (PV) devices are prepared based on the coevaporated rhombohedral AgBiI₃ films, with titanium dioxide (TiO₂) and poly(3-hexylthiophene) (P3HT) as electron- and hole-transport layers, respectively. The best-performing device exhibited a power conversion efficiency (PCE) of as high as 0.9% with open-circuit voltage (Voc) > 0.8 V in the reverse scan direction.
Combining perovskites with well-established photovoltaic materials such as silicon or CIGS is an attractive option for producing cheap, high efficiency and high voltage solar cells. Perovskite-based tandem solar cells can potentially achieve over 30% tandem efficiency. We demonstrate a 4-terminal tandem perovskite/silicon configuration in which the efficiency is as high as 26%, with 23.9% for a perovskite/CIGS tandem. We also demonstrate a two-terminal monolithic tandem device with a perovskite top cell and a polysilicon passivated c-Si bottom cell, with an efficiency of over 24%, using a novel approach that avoids the need for a dedicated interconnection layer. Much of the success of these approaches has come from the reduction of optical losses, and we discuss the potential for further progress in this direction. In addition we have found that a combination of PMMA and PCBM can provide effective interface passivation for perovskite solar cells, resulting in a Voc of over 1.2 V for a 1.6 eV bandgap perovskite cell. Finally we show an efficiency of over 20% for a perovskite cell using a CuPc hole transport layer, which demonstrates excellent thermal stability. These results show the clear potential of perovskites in practical high efficiency devices.

Efficient Wide-Bandgap Perovskite solar cells and the limiting factors of tandem solar cells efficiency, as parasitic absorption, reflection losses.

All-perovskite tandem cell has been considered as the potential candidate for bringing the power conversion efficiency (PCE) beyond the Shockley-Queisser limit of single-junction device and yet retaining the advantages of earth-abundant materials and solution processability. However, a challenging issue of realizing such solution-processed devices is the fulfillment of complex and coupled requirements of the interconnecting layer (ICL) including solvent-resistance to protect underlying perovskite film, high electrical properties for carrier transport and recombination, and high optical transmission. In this work, a new thermionic emission-based ICL with enhanced solvent-resistance feature is demonstrated. Fundamentally, the thermionic emission plays a critical role in the electron transport process in the ICL, which is confirmed through both experimental and theoretical studies. Besides achieving high optical transmission and electrical properties, the new ICL chemically protects the underlying perovskite film by introducing a fluoride silane incorporated polyethyleneimine ethoxylated (FSIP) hybrid system which also passivates the surface defects to reduce electrical loss. Our monolithic all-perovskite tandem solar cells demonstrate highest PCE of 17.9% [1]. Consequently, this work contributes to only understanding the fundamental mechanism of ICL but also to promoting robust and low-cost photovoltaics.


Strategies to Improve Perovskite on Silicon Tandem Solar Cells Performances Amalisa Bruno1,2, Herlina A. Dewi1, Wang Hao1, Kurt Vergeer1, Li Jia1, Lin Fern2, Maung Thway1, Armin Aberle3, Niran Mathews4 and Subodh Mhaisalkar5; "ERIS@N, Nanyang Technological University, Singapore, Singapore; 'SERIS, National University of Singapore, Singapore, Singapore.

The energy demand is constantly growing worldwide and Paris Agreement requirements of a substantial de-carbonization of electricity generation by 2050 are very stringent. Renewable energy production efficiencies need to be maximized to meet these urgent needs. Since solar irradiance is the largest resource of globally available energy, thus photovoltaics (PV) is in a prime position to deliver energy at costs similar to the fossil generated. Developing solar cells able to deliver high efficiencies, keeping their production cost and environmental impact low, would therefore address these issues. Nowadays, PV market is dominated by silicon solar cells delivering high efficiency and long-term stability. However, Si solar cells are approaching their practical efficiency limits and new methodologies are required to enhance SC power conversion efficiency. Tandem solar cells are the most promising and viable option for drastically improving the efficiency of existing PV technologies keeping the production cost low and versatile. 1,2 Indeed, combining Si solar cells with a low-cost wide-band-gap absorber material, as perovskite, it is possible to create tandem solar cells that efficiently absorb light in complementary regions of the solar spectrum and overcome the transmission and thermalization losses of a single junction solar cells. Research on perovskite on silicon tandem SCs is picking up very fast and in just three years very promising results have been reported on both four-terminal (4T), mechanically stacked, and two-terminals (2T), monolithically integrated tandem, silicon-perovskite tandem SCs. The development of high efficiency semi-transparent perovskite solar cells is critical for the implementation of high performing tandem solar cells.

In this work, we present tandem structures including semi-transparent perovskite with different band-gaps as top-cells and both hetero-junctions and passivated emitter and rear cell (PERC) silicon solar cells as bottom cells. Semi-transparent perovskite solar cells with different architectures have been developed and efficiencies above 16.0% with average transparency >80% in near-infrared have been demonstrated. Semi-transparent electrode has been realize by using sputtered indium tin oxide (ITO) as semi-transparent electrode and a thin Ag/MoOx buffer layer to protect the organic layers below and to guarantee the contact to be resistant to delamination but still highly transparent. 3 We will also present different solar cells realized both by spin-coating and thermal evaporation and strategies to improve their specific efficiencies. We will also discuss the effects of different perovskite bandgap solar cells and the limiting factors of tandem solar cells efficiency, as parasitic absorption, reflectance losses.

References

Efficient Wide-Bandgap Perovskite Solar Cells Enabled by Combining Bulk and Surface Passivation Strategies Cong Chen1,3, Chunxiaxiao Xiao1, Zhaoning Song1, Guojia Fang1, Chun-sheng Jiang2 and Yanfa Yan1; 1The University of Toledo, Toledo, Ohio, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States; 3Wuhan University, Wuhan, China.

Wide-bandgap (-1.7 to 1.9 eV) perovskite solar cells have attracted substantial research interest in recent years due to their great potential to fabricate efficient tandem solar cells via combining with a lower bandgap (1.1 to 1.3 eV) absorber (e.g., Si, CIGS, and low-bandgap perovskite). However, wide-bandgap perovskite solar cells usually suffer from large open circuit voltage ( VOC) deficits caused by small grain sizes and photoinduced phase segregation. Here, we introduce a small amount of Pb(SCN)2 as an additive into wide-bandgap FASn0.47C0.53PbI2.85Br0.15 perovskite precursor solution and simultaneously employing the solvent annealing method to fabricate high-quality wide-bandgap perovskite thin films. The synergetic effects of combining Pb(SCN)2 additive and solvent annealing strategies lead to enhanced grain size from ~200 nm to ~2 μm and creation of excess PbI2 to passivate defect states at grain boundaries. This advance enables an increase in the Voc of the p-n type perovskite solar cells from 1.12 to 1.21 V. Further, we adopt guanidinium bromide (GuaBr) solution to tune the effective doping and electronic properties at the back surface of perovskite thin films, which further enhance Voc to 1.24 V. The enhancement is attributed to the formation of a stronger electric field, revealed by Kelvin probe force microscopy (KPFM) measurements. With the optimization of the device fabrication process, we demonstrate a champion power conversion efficiency of 18.9% with a decent stability under continuous illumination.

High Efficiency and Flexible All-Perovskite Tandem Solar Cells Axel F. Palmstrom1, Tomas Leijtens1, Giles Eperon1, Rohit Prasanna2, Sanjini Nanayakkara3,
The emergence of metal halide perovskites as high efficiency, cost-effective solar materials has led to significant interest for perovskite-based tandems. Of existing perovskite-based tandem technologies, pairing wide-gap and low-gap perovskites in a monolithic all-perovskite tandem arguably offers the greatest potential by enabling efficiencies beyond the single-junction Shockley-Queisser limit with low-cost solution processing on a flexible, lightweight substrate. As of yet, efficiency of all-perovskite monolithic tandems has lagged behind perovskites paired with silicon or CIGS despite significant improvement to low-gap perovskite materials. The state-of-the-art all-perovskite 2T tandems have been limited by several main factors: 1) relatively low fill factors, 2) shunting due to the use of a thick (100nm) and conductive recombination layer of indium tin oxide allowing lateral connectivity of shunt pathways in either subcell, and 3) large voltage losses in the wide gap subcell due to photoinduced halide segregation, resulting in lower than ideal voltages for the tandem overall. Here, we develop strategies to overcome all of these issues and attain record-efficiency all-perovskite tandem devices.

We have substantially improved the recombination layer with an ultra-thin nucleophilic surface modification to C60 for improved atomic layer deposition (ALD), enhancing the solvent/sputter barrier properties and mechanical stability of ALD-grown recombination layers. This strategy enables the fabrication of recombination layers that are thinner and less laterally conductive (reduced shunting) than currently reported strategies. Secondly, we improve the voltage of our wide-gap cell through A-site cation bandgap tuning. A combination of large and small A-site cations are used to tint the metal halide octahedral. This increases the bandgap and therefore reduces the amount of bromine needed to attain a certain bandgap. We achieved a band gap of 1.7eV with a solution bromide concentration of only 20%. We find that this strategy results in higher voltages and efficiencies 20%. We have also demonstrated two-terminal all-perovskite tandems with efficiencies over 23% for rigid devices and 21% for flexible devices.

8:30 AM ES16.12.01
Enhancement of Efficiency for Sn Perovskite Solar Cells (Pb free) by Reducing Lattice Strain
Kohei Nishimura1, Daisuke Hirotani1, Muhammad Akmal Kamarudin1, Satoshi Ikubo1, Qing Shen1, Minemoto Takashi2, Kenji Yoshino3 and Shuzi Hayase1,2,4,5
1Kyushu Institute of Technology, Kitakyushu, Japan; 2University of Electro-communications, Cho-fu, Japan; 3Ritsumeikan University, Kusatsu, Japan; 4Miyazaki University, Miyazaki, Japan.

Sn perovskite solar cell is one of the most expected Pb-free perovskite solar cells with high efficiency. We have already reported the efficiency of SnGe-perovskite with 7.9%. It has been also reported that Sn perovskite solar cell efficiency was enhanced to over 9% by inserting 2D structure partially. It is well known that the stability of perovskite structure is expected by Tolerance Factor. In the research on enhancing the Sn-perovskite solar cells, we focused on the relationship between the lattice strain of the Sn-perovskite calculated from XRD data and the solar cell efficiency. Sn perovskite solar cell is expressed as ASnI3, where A stand for cation. In this research, we employed (B0.1)(FA0.75MA0.25)0.9SnI3, where A cation is the mixture of (B0.1)(FA0.75MA0.25)0.9. In this report, B was varied was varied from small Na cation to large Butyl ammonium cations (Na cation, K cation, Et ammonium cation and Butyl ammonium cation). The lattice strain decreased with an increase in the ion radius from Na, K, Cs, Et ammonium, and Butyl ammonium. Replacement of FAA with Et ammonium cation gave smallest lattice strain. By introducing Bu ammonium cation, the lattice strain increased with keeping the 3D structure at 5 mol %. By the addition of 10, and 20% addition, the strain decreased with the formation of 2D structure as it is well-known in the literature. Therefore, estimation of lattice strain by XRD peaks was proved to be useful. The solar cell efficiency had good correlation with the lattice strain. Low lattice strain gave high efficiency when MAFA was partially replaced by from Na ion to Ethyl ammonium cation. Introduction of Et ammonium ion with the smallest lattice strain gave the best results. The relative lattice strain of FA0.75MA0.25SnI3 was 0.057 (Tolerance factor: 0.979). When 10 mol % of Et ammonium cation was introduced, the relative lattice strain decreased to 0.035 (tolerance factor:0.985), the efficiency of the solar cells was enhanced from 2.34% without adding Et ammonium cation to 3.72% with 10 mol% addition. The efficiency was saturated at 20mol % concentration (3.45%). XRD signal showed that 3D structure was held and the increase in the efficiency was not explained by the insertion of 2D structure which has been reported before. All of the FF, Jsc, and Voc increased with a decrease in the lattice strain. By introducing 10% of EtA cation, the efficiency of solar cells consisting of TIO/PTCDA/PSS:EA0.1[(FA0.75MA0.25)0.9SnI3](PCBM:60) was enhanced to 5.41 %. Sn perovskite solar cells with 7.9% is reported.

8:45 AM ES16.12.02
Bandgap Modulation in Cs-Pt-I-O Perovskites Based on Solvent Engineering
Dakota Schwartz1 and Shubhra Bansal1; University of Nevada, Las Vegas, Las Vegas, Nevada, United States.

Organic-inorganic hybrid perovskite solar cells have attracted immense attention because of excellent optoelectronic properties and record power conversion efficiency (PCE) has surpassed 23.3% within a few years. Despite the very high efficiency already attained by HPSCs (ABX3; A = MA, FA, Cs; B = Pb,Sn; X=I, Br, Cl) resulting from high absorption coefficient and electron-hole diffusion lengths, toxicity of Pb and stability of these materials are veritable issues. Composition space for Pb-free perovskite ABX3 is expected by Tolerance Factor. In the research on enhancing the Sn-perovskite solar cells, we focused on the relationship between the lattice strain of the Sn-perovskite calculated from XRD data and the solar cell efficiency. Sn perovskite solar cell is expressed as ASnI3, where A stand for cation. In this research, we employed (B0.1)(FA0.75MA0.25)0.9SnI3, where A cation is the mixture of (B0.1)(FA0.75MA0.25)0.9. In this report, B was varied was varied from small Na cation to large Butyl ammonium cations (Na cation, K cation, Et ammonium cation and Butyl ammonium cation). The lattice strain decreased with an increase in the ion radius from Na, K, Cs, Et ammonium, and Butyl ammonium. Replacement of FAA with Et ammonium cation gave smallest lattice strain. By introducing Bu ammonium cation, the lattice strain increased with keeping the 3D structure at 5 mol %. By the addition of 10, and 20% addition, the strain decreased with the formation of 2D structure as it is well-known in the literature. Therefore, estimation of lattice strain by XRD peaks was proved to be useful. The solar cell efficiency had good correlation with the lattice strain. Low lattice strain gave high efficiency when MAFA was partially replaced by from Na ion to Ethyl ammonium cation. Introduction of Et ammonium ion with the smallest lattice strain gave the best results. The relative lattice strain of FA0.75MA0.25SnI3 was 0.057 (Tolerance factor: 0.979). When 10 mol % of Et ammonium cation was introduced, the relative lattice strain decreased to 0.035 (tolerance factor:0.985), the efficiency of the solar cells was enhanced from 2.34% without adding Et ammonium cation to 3.72% with 10 mon% addition. The efficiency was saturated at 20mol % concentration (3.45%). XRD signal showed that 3D structure was held and the increase in the efficiency was not explained by the insertion of 2D structure which has been reported before. All of the FF, Jsc, and Voc increased with a decrease in the lattice strain. By introducing 10% of EA cation, the efficiency of solar cells consisting of TIO/PTCDA/PSS:EA0.1[(FA0.75MA0.25)0.9SnI3](PCBM:60) was enhanced to 5.41 %. Sn perovskite solar cells with 7.9% is reported.

9:00 AM ES16.12.03
Highly Stable and Efficient All-Inorganic Tin-Based Halide Perovskite Solar Cells
Min Chen1, Minggang Ju2, Xiao C. Zeng3, Yuan yuan Zhou1 and Nitin P. Padture1, 3Brown University, Providence, Rhode Island, United States; 2Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

The state-of-the-art high efficiency perovskite solar cells (PSCs) contain lead and organic cations in the perovskite light-absorber. However, the toxicity associated with the lead and the volatility of the organic cations are hurdles in the path towards the future commercialization of PSCs. While there has been effort towards replacing lead cation with less toxic cations, typical lead-free PSCs still suffer from the low power-conversion efficiency (PCE) and poor stability. Herein, we have utilized an alloying strategy in all-inorganic Sn-based perovskite materials, and realized PSCs with a promising PCE of up to 7.11%. Furthermore, the formation of a stable, robust native-oxide layer passivates the surface resulting in superior air-stability, with <10% PCE decay after 500 hours continuous operation under one-sun illumination. Thus, this work provides a new avenue for the design and development of high performance and stable Sn-based PSCs.

SESSION ES16.12: Reducing Lead and Perovskite-Inspired Materials
Session Chairs: Nakita Noel and Pankaj Yadav
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 125 AB
Hybrid organic-inorganic perovskite (HOIP) solar cells – particularly those using $\text{APbX}_3$ [$\text{A} = \text{CH}_3\text{NH}_3$, HC(NH$_3$)$_2$, Cs$^+$ and X = I$^-$, Cl$^-$, Br$^-$] as the absorber layer – have already exceeded the 23% conversion efficiency milestone, surpassing the record efficiencies of well-established photovoltaic technologies based on multicrystalline silicon, c-Si, and cadmium telluride absorbers [1]. However, a major obstacle in the commercialization of HOIP-based solar devices continues to be their short operational lifetimes, with significant performance decreases observed within the first hours in service [2]. Because this deterioration is linked to the intrinsic instability of the HOIP [3], reducing their defect concentrations seems a key strategy towards improving the long-term stability of this type of absorber and, therefore, of solar devices produced from them. Recently, it has been shown that the addition of divalent cation halide salts (e.g., SrI$_2$ and MgI$_2$) to the HOIP precursor mixture yields thin-films with lower defect concentrations, leading to boosts in resulting solar device performance [4,5]. The additives are expected to increase halide content, thus effectively filling halide vacancies, however an understanding of the doping role of the divalent cation and the mechanism inducing the observed device improvements is, at best, incomplete.

Using hard x-ray photoelectron spectroscopy (HAXPES), we have investigated the chemical and electronic structure of a Sr-doped MAPbI$_3$ thin-film sample prepared by varying the concentration of SrI$_2$ additive within a 0 to 2 mol% range. Sr is detected in all Sr-doped samples, and depth-dependent measurements reveal a pronounced surface accumulation of Sr in samples with higher Sr-doping concentrations, suggesting a Sr lattice incorporation saturation. Moreover, significant reductions in defect states (i.e., Pb$^0$) are detected for all Sr-doped samples compared to (undoped) MAPbI$_3$. The effect of the Sr-doping concentration and detected Pb$^0$ defect changes on the electronic structure is discussed in this contribution, as well as a comparison of the chemical and electronic properties with the device performance (enhancements) of corresponding solar cells.


9:50 AM ES16.12.05


Lead-free double-perovskites (A$_2$M$^+$M$^-X_6$) have been recently proposed as a stable and environmental friendly alternative to lead-based perovskites. Among the vast number of possible double-perovskite compositions, Cs$_2$AgBiBr$_6$ has been the most investigated material, both from a theoretical and experimental point of view. To date, the majority of fundamental studies on this material have been conducted on single crystals or powders, which is due to the poor solubility of the material precursors and to difficulties in obtaining smooth and uniform films. Vapour deposition offers to be a promising alternative for the formation of Cs$_2$AgBiBr$_6$ films, overcoming the drawbacks of traditional solution chemical methods and time-consuming growth of single crystals. In particular, physical vapour deposition can produce high-quality films with various thicknesses and smooth surfaces. In this way, numerous spectroscopic techniques which require non-scattering surfaces (like TRPL or THz spectroscopy), as well as thickness- and temperature-dependent transient photoconductivity measurements can be conducted to get an insight in the optoelectronic properties of the material. Here, we disclose our recent findings on vapour-deposited Cs$_2$AgBiBr$_6$, demonstrating not only efficient double-perovskite solar cells, but also presenting a fundamental understanding of the carriers dynamics in the double-perovskite thin films, not achievable otherwise.

9:45 AM ES16.12.06

High Performance Low Dimensional Tin Perovskite Solar Cells Zhijun Ning, Fei Wang and Xianyuan Jiang; ShanghaiTech University, Shanghai, China.

The low toxicity and a near-ideal bandgap make tin (Sn) perovskite an attractive alternative to lead perovskite for next generation solar cells. However, the development of Sn perovskite is still an emerging field in which fundamental studies on this material have been conducted on single crystals or powders, which is due to the poor solubility of the material precursors and to difficulties in obtaining smooth and uniform films. Vapour deposition offers to be a promising alternative for the formation of Cs$_2$AgBiBr$_6$ films, overcoming the drawbacks of traditional solution chemical methods and time-consuming growth of single crystals. In particular, physical vapour deposition can produce high-quality films with various thicknesses and smooth surfaces. In this way, numerous spectroscopic techniques which require non-scattering surfaces (like TRPL or THz spectroscopy), as well as thickness- and temperature-dependent transient photoconductivity measurements can be conducted to get an insight in the optoelectronic properties of the material. Here, we disclose our recent findings on vapour-deposited Cs$_2$AgBiBr$_6$, demonstrating not only efficient double-perovskite solar cells, but also presenting a fundamental understanding of the carriers dynamics in the double-perovskite thin films, not achievable otherwise.

References

10:00 AM BREAK

10:30 AM ES16.12.07

Improved Charge Carrier Lifetimes with Partial Substitution of Lead with Strontium in Perovskite Compounds Aditya S. Yerramilli1; Yuancheng Chen2; Yang Song1, 2 and Terry Alford1; 1Arizona State University, Tempe, Arizona, United States; 2Materials Physics and Chemistry, X’ian University, X’ian, China; 3Materials Science, African University of Science and Technology, Abuja, Nigeria.

Lead (Pb) based perovskite solar cells have come a long way since their inception. However, toxicity issues due to the presence of lead have adversely affected their commercial potential. Strontium (Sr) a relatively non-toxic element is a viable candidate to replace Pb, given the similar ionic radius (Sr$^{2+}$ = 132 pm, Pb$^{2+}$ = 133 pm). We have prepared samples using accurate-based precursors to make devices with different substitution percentages of Pb with Sr, of 10% and 20%. We have obtained a reasonable device efficiency of 8.9% and 5.7% for 10% and 20% substitution devices, respectively. Charge carrier lifetimes gave 117.91ns for 10% and 109.36ns for 20% samples which are higher compared to the 103.79ns for a complete Pb based control device. Higher order substitution of Pb with more than 20% Sr has however resulted in a poor performance which can be due to the formation of SrO, Sr$_2$(C$_2$H$_5$O$_3$)$_3$, and SrCO$_3$ compounds which act as barriers for smooth charge transport.

10:45 AM ES16.12.08

All-Solution-Processed Organic/ Inorganic Hybrid Perovskite Nanocrystalline Photodetectors Guodan Wei, Jingzhou Li1 and Feiuyu Kang1; 1Graduate School at Shenzhen, Tsinghua University, Shenzhen, China; 2Tsinghua-Berkeley Shenzhen Institute, Tsinghua University, Shenzhen, China.

Recently, inorganic lead halide perovskite nanocrystals show great potential in infrared, visible and multispectral photodetectors (PD) for sensing, security and electronics applications. Considerable progress has been obtained through solution-processed fabrication technique which combines ease of processing, tailorable optoelectronic properties, facile compatibility with flexible structures. However, the stability of the nanocrystals in ambient condition has always been a great challenge in as-prepared PDs. In this work, an air stable organic/inorganic hybrid lead halide perovskite nanocrystalline PD has been obtained from full solution processes, using Cs$_2$PbBr$_4$ quantum dots (QDs) as the photocative layer, Poly(N, N-hexyl-4-butylphenyl)-N,N'-bisphenyl benzidine (poly-TPD) and phenyl-C61-butyric acid methyl ester (PCBM) as the electron transport/hole blocking
layer (ETL/HBL). The resulting device has significantly suppressed dark current as low as 10 nA/cm². The responsivity of greater than 1 A/W was obtained for this unique hybrid structure, and it has been approved up to one order of magnitude enhancement when compared with the device without the organic combination layers of poly-TPD and PCBM. Especially, these as-prepared devices remain stable for more than one week even without encapsulation. In this solution process, hydrofluoroethers (MT700) was employed as an effective protective layer for QD nanocrystals. Further, we systematically studied the influence of different types of organic carrier transport layers on device performance.

11:00 AM ES16.12.09 Reducing Saturation-Current Density to Realize High-Efficiency Low-Bandgap Mixed Tin-Lead Halide Perovskite Solar Cells Chongwen Li, Zhaoning Song and Yanfa Yan; The University of Toledo, Toledo, Ohio, United States.

The unsatisfactory performance of low-bandgap mixed tin (Sn)-lead (Pb) halide perovskite subcells has been one of the major obstacles hindering the progress of the power conversion efficiencies (PCEs) of all-perovskite tandem solar cells. By analyzing dark-current density and distribution, we identified that charge recombination at grain boundaries is a key factor limiting the performance of low-bandgap mixed Sn-Pb halide perovskite subcells. We further found that bromine (Br) incorporation can effectively passivate grain boundaries and lower the dark current density by two-three orders of magnitude. By optimizing the Br concentration, we successfully fabricated low-bandgap (1.272 eV) mixed Sn-Pb halide perovskite solar cells with open-circuit voltage deficits as low as 0.384 V and fill factors as high as 78%. The best-performing device showed a PCE of >19%. Our results suggest an important direction for improving the performance of low-bandgap mixed Sn-Pb halide perovskite solar cells.

11:15 AM ES16.12.10 Efficient Defect Removal and Passivation of Pb-Sn Mixed Perovskites Enabling High Performing Solar Cells with High Charge Carrier Mobilities and Fill Factors of 83% Indrachapa Bandara R M, Imalka Jayawardana, Steven Hinder, Stephanie Adeyemo, Hannah Joyce, Radu Sperlea and Ravi Silva; 1University of Surrey, Guildford, United Kingdom; 2Engineering Department, University of Cambridge, Cambridge, United Kingdom.

In realizing new materials for low cost, high performance, solution processed photovoltaic (PV) devices, metal halide perovskites continue to show increasing potential. To enable solution processed tandem PVs by tuning the bandgap, as well as reducing the toxicity of conventional Pb-based perovskites solar cells (PSCs), Pb-Sn mixed perovskites have recently shown excellent capability (Eperon et al. Science 354, 861). However, one of the prevailing issues in these PSCs is the fast oxidation of Sn⁴⁺ to Sn²⁺ giving rise to a “self-doping” process (Noel et al. Energy Environ. Sci. 7, 3061). Sn²⁺ dopants play a major role in non-radiative recombination in Sn-based perovskites by acting as trap sites for mobile photo-generated charge carriers. This has made it difficult for these PSCs to have comparable efficiencies with Pb-only perovskites. Although there have been efforts to inhibit the oxidation process, most commonly with the addition of SnF₂ (Leijtens et al. ACS Energy Lett. 2, 2159), there are no known studies reported on the complete removal of Sn²⁺ defects.

Interestingly, it has been reported that the efficient extraction of Sn⁴⁺ from ionic mixtures in ores, alloys and food is dependent on the solvent system used. Based on this premise, we investigate a solvent extraction method to achieve the complete removal of Sn⁴⁺ through anti-solvent engineering for Sn-based perovskites, on a novel triple cation Pb-Sn mixed perovskite system with the formula CsₓPb₁₋ₓSnₓI₄ (Sn bandgap 1.26 eV). The THz photoconductivity studies show high charge carrier mobilities for solvents which enable the highest Sn⁴⁺ extraction resulting in a maximum of 23.52 cm² V⁻¹ s⁻¹, the highest observed for Sn-based PSCs. This trend continues in XPS surface analysis which indicates a clear dependence on the anti-solvent used. The most efficient Sn⁴⁺ extracting solvent also enables the highest grain sizes, lowest Urbach energies and highest PSC performance leading to champion PCE 11.62%. This is an 80% improved compared to other anti-solvents that extract Sn⁴⁺ less efficiently. Significant improvements were observed for the Jₚ, where the highest value observed is 28.05 mA cm⁻² for the best performing devices compared to the highest values for the other two solvents tested in this work, 22.10 mA cm⁻² and 21.48 mA cm⁻², while dark leakage current is minimal with when Sn⁴⁺ is more efficiently extracted. Sn²⁺ is seen to act as shallow traps, as evident from the dark current analysis. Further strengthening the argument that solvent engineering aids in Sn⁴⁺ removal, the Pb-only analogue of the PSCs did not show a performance dependence on the anti-solvent used.

Next, we introduce a mechanism by which Sn⁴⁺ is extracted through complex formation with the optimized solvent extraction medium used. Building on this foundation, the complete removal of Sn⁴⁺ was achieved by tuning the solvent engineering process and annealing temperature. Finally, the performance is further enhanced by defect passivation by fabricating a wide bandgap perovskite structure at the grain surfaces, leading to efficiencies towards 15%. Here, we achieve 83% fill factor, which is the highest achieved for a Sn-based perovskite and strongly competes with the Pb-only PSCs.

11:30 AM ES16.12.11 Solution-Processed Lead-Free Double Perovskites Exhibit Potential for Photovoltaics with Narrowed Bandgaps Yuan Liu, Li Zhang and Hongwei Zhu; 1Tsinghua University, Beijing, China; 2Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China.

To date, while solar cells (SCs) have been developed for years with striking advancement especially in silicon SCs and perovskite SCs, a new issue has been emerging in such progress: how to manufacture SCs in an environmental-friendly way with the help of non-toxic and durable materials. Taking such environmental consequences into consideration, recently, double perovskites AₓBCₓ₂ (A=Cs, Bi; Ag, Cu, In, C=In, Bi, Sb, X=Cl, Br, I) have provoked substantial interests among researchers, especially those who are eager to solve the toxic and unstable nature of lead halide perovskites. Since the capacity of the perovskite SCs for reaching high power conversion efficiencies has been widely revealed, it is of great potential that the AₓBCₓ₂ double perovskites would substitute the traditional perovskites for SCs in the future.

Continuous researches have revealed that Cs₂AgBi₂I₇, though the processability and stability of which are favorable, has a relatively wide and intrinsically indirect bandgap which seems unsuitable for photovoltaics. To solve such problem, we pick up Cs₂AgBi₂I₇, double perovskite as the matrix and, herein, report a feasible method for the synthesis of Cs₂AgSb₂Bi₁₋ₓBrₓ, through the solution process, where antimony serves as the alloying element for narrowing the bandgap. Apart from former synthetic method through a time- and energy consuming process at over 300°C, in this work, we successfully dissolved the precursors in the dimethylsulfoxide in a short time then fabricated double perovskites thin films directly and quickly on the prepared substrates. Meanwhile, we also tested the thermostability and reliability of the thin films under different conditions, as well as the photovoltaic properties and the band structure. Further, following a similar methodology of traditional perovskite SCs researches, we conducted an advanced study on the performance of the Cs₂AgSb₂Bi₁₋ₓBrₓ SCs. Conclusively, our results suggest that feasibility of controlled synthesis of Cs₂AgSb₂Bi₁₋ₓBrₓ thin films and indicate that Cs₂AgSb₂Bi₁₋ₓBrₓ double perovskites, benefited from its narrowed bandgap, would be more applicable as the photovoltaic layer in SCs or photodetectors.

11:45 AM ES16.12.12 Impact of Composition and Structure on Bismuth Halide Perovskites Rainie Nelson, Bradley J. Ryan, Atefe Hadi, Umar Hamdeh, Matthew Milot and Matthew G. Panthani; Iowa State University, Ames, Iowa, United States.

Bismuth halide perovskites have shown rapid advancements in power conversion efficiencies over a decade, leading to an increased focus in these materials for solar cells and other optoelectronics. However, stability issues and the unavoidable toxicity of lead prove potential barriers to large-scale applications and implementations of the lead halide perovskites. Bismuth has long been a replacement for lead in various applications, and some of the similarities in electronic properties make bismuth an interesting candidate to replace lead for optoelectronic materials. In this work, we describe bismuth halide perovskite and perovskite-inspired materials which demonstrate a wide range of properties. We show photoluminescence of bismuth halide precursor seeds in the synthesis of cesium bismuth halide nanocrystals, absorbance tunability of cesium bismuth halide nanocrystals based on halide composition, thermochromism of a layered double perovskite and the apparent sonocrystallization of nanocrystals from bulk crystals of layered double perovskites of various compositions. We identify promising properties of these perovskite materials and discuss major areas that require investigation in order to make bismuth halide perovskites viable materials for a variety of applications.
Lithium-Free Radical Triarylamine Dopsants for Small Molecule-Based Organic Hole-Transport Layers in Perovskite Solar Cells—Impact on Device Performance and Stability

Trapey H. Schloezer1,2, Timothy Gehan4, Jeffrey Christian3, Debbie Mitchell2, Alex Dixon2, Zhen Li3, Kai Zhu2, Joseph Berry3, Joseph Luther4 and Alan Sellinger3,5,6, Colorado School of Mines, Golden, Colorado, United States; 2Hope College, Holland, Michigan, United States; 3Northwestern Polytechnical University and Shaanxi Joint Laboratory of Graphene (NPU), Xi'an, China; 4National Renewable Energy Laboratory, Golden, Colorado, United States; 5University of Denver, Denver, Colorado, United States; 6University of Nova Gorica, Nova Gorica, Slovenia.

Within the PSC device stack, charge-selective contact selection has been shown to considerably impact PSC stability. Recently, a triarylamine-based hole-transport layer (HTL) doped with its oxidized organic salt analogue (EH44/EH44-ox) has been shown to bypass the need for hygroscopic lithium salt dopants, enabling high PSC stability in ambient conditions and room temperature. However, as the improved stability came with a power conversion efficiency (PCE) penalty, and stability suffered at elevated temperatures. Broadening the applicability and understanding of this under-utilized HTL dopant system, we report design criteria for stable, synthetically simple triarylamine-based organic hole transport materials (HTM) and their corresponding oxidized salts as HTL dopants for improved PSC efficiency and stability at elevated temperature. The triarylamine-based dopants must contain at least two para-electro donors for radical cation stabilization to prevent impurity formation (e.g., dopant reduction) which significantly reduces PSC fill factors (FF). Furthermore, these dopants can be interchanged with respect to the HTL matrix for improved PSC FF and PCE. The stability of devices (unencapsulated in ambient atmosphere under constant load and illumination) prepared with these three new HTLs considerably outperform both EH44/EH44-ox and Li1-doped spiro-OmeTAD controls at 50 and 70 °C. The ability to mix and match a dopant stable with a non-identical small-molecule-based HTL matrix for improved charge-transport properties has broadened the design scope for highly stable and cost-effective PSC without sacrificing performance. This is collaborative work with the National Renewable Energy Lab (NREL).

Highly Stable Carbon-Based Perovskite Solar Cell with an Efficiency of over 18% via Hole Transport Engineering

Qianqian Chu1,2, Xi'an Jiaotong University, Xi'an, China; 1Material science and engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Carbon-based perovskite solar cells show great potential owing to their low-cost production and superior stability in air, compared to their counterparts using metal contacts. The photovoltaic performance of carbon-based PSCs, however, has been progressing slowly in spite of an impressive efficiency when they were first reported. One of the major obstacles is that the free energy change for hole-extraction from the perovskite layer, while TPAs about the conjugated fluorene moiety increase the free energy change for hole-extraction from the perovskite layer, two orders of magnitude larger than pure P3HT. The improved charge transport and extraction provided by the composite HTL provides a significant efficiency improvement compared to cells with a pure P3HT HTL. As a result, we report carbon-based solar cells with a record efficiency of 17.8% (certified by Newport); and the first perovskite cells to be certified under the stabilized testing protocol. The stability of devices (unencapsulated in ambient atmosphere under constant load and illumination) prepared with these three new HTLs considerably outperform both EH44/EH44-ox and Li1-doped spiro-OmeTAD controls at 50 and 70 °C. The ability to mix and match a dopant stable with a non-identical small-molecule-based HTL matrix for improved charge-transport properties has broadened the design scope for highly stable and cost-effective PSC without sacrificing performance. This is collaborative work with the National Renewable Energy Lab (NREL).
systems for space applications is evidenced by the lack of any phase transition between 4.2 K and 300 K, which demonstrates the excellent stability of these mixed cation perovskites. Temperature and intensity dependent current density-voltage (J-V) measurements are used to probe the solar cells under conditions consistent with the environments around the outer planetary systems of Mars, Jupiter, and Saturn. At low temperature, a barrier impeding current flow is observed in the structure and results in a largely decreased fill factor under 1-Sun AM0 conditions. However, under low intensity and low temperature (LILT) conditions, the fill factor and the power conversion efficiency are recovered. At low temperature, thermionic emission is the limiting factor for carrier extraction over the barrier and as such the short photocurrent generated at LILT conditions provide the conditions for efficient carrier extraction, even in situations where sample degradation may have occurred in transit.


3:35 PM ES16.14.02
Perovskite Quantum Dot Photovoltaics—Ligand Chemistry, Optoelectronics and Charge Transport for High Voltage Solar Cells Mokshin Suri1, Abhijit Hazarika1, Lance Wheeler1, Bryon Larson2, Joseph Luther2 and Brian A. Korgel1; 1The University of Texas at Austin, Austin, Texas, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Improving the open-circuit voltage (Voc) of photovoltaic devices (PVs) made with wide-bandgap (Eg≥1.8 eV) perovskites is a major goal in the development of low-cost, high-efficiency tandem solar cells that use these materials as a top cell. There is significant interest in using perovskite quantum dots (PQDs) for this application. PVs made with CsPbI, PQDs with Eg≥1.75 eV now hold the record power conversion efficiency (13.4%) for all quantum dot materials. PQD PVs show higher Voc than PVs made with similar bulk perovskite composition, and further, it is easy to manipulate the bandgap of the PQDs by synthetically tuning their size and composition. To date, however, PQD solar cells with Eg≥1.8 eV have exhibited poor device performance, due especially to high voltage loss. To alleviate these problems, we have sought to develop PQD ligand chemistry that enables high efficiency PQD device fabrication. We have found that the performance of wide bandgap PQD PVs correlates with the photoluminescence (PL) lifetime and carrier diffusion length of the PQD layer, and that the performance of wide bandgap PQD PVs can be significantly improved with appropriate modifications of the PQD composition and surface chemistry. For instance, the exchange of native oleate and oleylammonium ligands with acetic acid and formamidinium significantly increases the carrier mobility, enabling devices with high Voc. We found that PQD PVs made from CsPbI1-xBrx and FAPbI1-xBrx with sufficiently wide bandgap for tandem devices exhibit decreased Voc, short PL lifetimes, and decreased carrier diffusion lengths due to the high Br incorporation required for bandgap tuning. PL lifetime and carrier diffusion length of wide bandgap PQDs can be improved by mixing FA and Cs at the A-site, i.e., (FA1-xCsx)PbI3. Alloying of FA and Cs at the A-site balances Br incorporation at the X-site to yield wide bandgap PQD PVs with improved Voc. This work highlights potential strategies for producing the high-voltage, wide bandgap perovskite photovoltaic devices needed for a next generation of high efficiency tandem devices.

3:30 PM ES16.14.03
Design and Implementation of Information Pipeline for Robot-Ready Perovskite Experimental Data Acquisition Ian M. Pendleton1, Mansoor Ani N. Neillikal1, Zhi Li1, Emory M. Chau1, Alex Norquist1 and Joshua Schrier1; Haverford College, Haverford, Pennsylvania, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Fordham University, New York, New York, United States.

Design of new crystalline materials requires understanding the relationship between physical inputs of a system, such as chemicals, conditions, and molecular features, and the corresponding results. The chemical processes underlying crystallization in relatively simple systems can be confounded through small changes in solution concentrations, temperatures, or stochastic effects. Statistical models, such as machine learning, can aid in quantifying relationships between variations in chemical environment and reaction outcome. For success, statistical models targeting real-time data collection generally require data pipelines that assemble normalized datasets. Toward this end, we have developed a platform which brings together data storage, hardware/software interface, and simple experimental user interfaces into a single data pipeline. The key components of this pipeline include: generation of initial search parameters and robotic input files, accessible interfaces for data input by experimentalists, and in-line molecular feature calculations. Discussion topics will include the process for navigating the large initial experimental search space including automated physical constraints as well as user specifications, development of the technology stack to aid in data acquisition, and the resulting chemical ontology used to describe the underlying relationships between the chemistry and the data will be discussed. Particular attention will be given to what has emerged as ‘best practices’ for data curation, acquisition, and the development of a scalable workflow. An overview on the development and application to organohalide perovskite crystal formation will be discussed, and the work needed to implement similar processes for disparate chemical systems with moderate adjustment will be highlighted. This work provides an overview of the tools necessary for further development of real-time data capture in materials chemistry and outlines the first steps to construct larger databases for use in materials discovery.

3:45 PM ES16.14.04
High Performance Hybrid Perovskite Based Photodetector on Flexible Substrate for Wearable Sensor Applications Son Singh, Rahim Abdur, Md Abdul Kuddus Sheikh and Jaegab Lee; Kookmin University, Seoul, Korea (the Republic of).

Excellent flexibility with high mechanically stable of photonic devices are essential for next-generation integrated optoelectronic systems, wearable sensors and flexible consumer electronics. Here we describe hybrid perovskite based flexible photodetector for wearable sensor devices. The hybrid perovskites are excellent new materials with high carrier mobility, high photo conversion efficiency, tunable bandgap and excellent optoelectronic properties. These materials have advantage of low temperature and easy processing, and facile scale-up. In this study, we discuss the design and experimental demonstration of hybrid perovskite based photodetector integrated on flexible sensor platform. We have fabricated perovskite-based flexible photodetector consisting of ITO/CdS/perovskite/V1O5/Au, focusing on the conformal coating of perovskite on the planar CdS by addition of PbBr2 and PbCl2 to PbI2, which significantly increases the nucleation rate of perovskite-leading to highly smooth surface morphology of perovskite. This enhances the performance of photodetectors. The devices are fabricated on flexible PEN substrate which are withstand many bending cycles at a submillimeter radius without degradation of optoelectronic properties. Our findings provide a hybrid perovskite sensor platform for photonic devices to improve their role in the area of flexible and mechanically stable optoelectronic systems.

4:00 PM ES16.14.05
Photovoltaic Efficiency of CsPbI3 Quantum Dots-Based Solar Cell Exceeding 14% Yueli Liu; State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China.

The emergence of organic-inorganic hybrid lead halide perovskites has received the impressive power conversion efficiency (PCE) over 22% within a few years [1]. However, the long-term stabilities of perovskite materials, including the durability under humid, thermal, UV radiation and other environmental conditions, are still poor due to the organic components, which are becoming to be the major challenges for their commercialization [2]. α-CsPbI3, as an all-inorganic lead halide, has been reported recently and exhibited excellent optoelectronic property and good stability, which is regarded as an outstanding alternative to organic-inorganic hybrid lead halide perovskites and a promising light-harvesting absorber for solar cell application [3]. Quantum dot-induced phase stabilization is believed to be an effective procedure to get α-CsPbI3 and suppress the formation of orthorhombic phase (6) CsPbI3. Protescu et al. have provided a hot-injection method for the preparation of high quality α-CsPbI3 quantum dots (QDs) [4]; α-CsPbI3 QDs based solar cells are reported by Luther and co-workers subsequently, which achieve a high PCE over 13% [5]. However, the short-circuit current density (JSC) is still low at present, which restricts the performance of CsPbI3 —based solar cells. In the work, α-CsPbI3 QDs were prepared by hot-injection method, and high performance inorganic perovskite quantum dot-based solar cells over 14.65% was fabricated, and the optimized device achieved a highly reproducible champion PCE of 13.05% with a high short-circuit current density (18.68 mA cm−2). This work provides an effective strategy for boosting high performance for all-inorganic lead halide PSCs.
Beyond Solar Cells—Perovskite Radiation Detectors and Light Emitting Diodes

Jinsong Huang; University of North Carolina-Chapel Hill, Chapel Hill, North Carolina, United States.

The excellent optoelectronic properties of halide perovskite materials and the easy growth of single crystals from solution make them ideal candidates for other electronic devices beyond solar cells. Here we will report the birth of perovskite radiation detectors, and advances in imaging detectors in terms of scaling up and integration with silicon read-out circuitry. Single photon detectors will also be presented to outline the challenges and opportunities for perovskite materials. Finally, we will present recent progress in making perovskite to be very efficient blue emitters.

Chemistry and Devices from Halide Perovskites Semiconductors

Merceauri G. Kanatzidis; Northwestern University, Evanston, Illinois, United States.

Two-dimensional (2D) metal halide perovskites have made an impressive entry in the field of solar cells and LEDs as highly promising semiconductors. They feature a high degree of structural flexibility and tunable optoelectronic properties. They have a general formula of (A’)3+(A)n–(MXy)3n+1, where A = Cs+, CH3NH3+(MA), H(CN)3H2+(FA), M = Ge2+, Sn2+, Pb2+ and X = Cl, Br, I, are the perovskite components and A’ = RNH3 is an organic spacer. There are four kinds of 2D organic inorganic hybrid perovskites so far: Ruddlesden-Popper, Cation-ordered, Jacobson-Dion and Diammonium Cation. These vary from one another in ways the inorganic slabs stack and the way the spacer cations interact with the inorganic slabs. Generally, 2D perovskites form from solution via the bottom-up self-assembly of individual, semiconducting perovskite sheets having an adjustable slab thickness of up to few nanometers, separated by insulating bulky organic molecules. As a result, they behave as natural multiple quantum wells (QWs) with the semiconducting perovskite layers representing the wells and the insulating organic spacers representing the barriers. The width of the barrier is fixed and depends only on the length of the A’ cation, while the width of the well can be adjusted by varying the thickness of perovskite slabs, which is defined by the n variable in (A’)3+(A)n–(MXy)3n+1. It is critical to understand the thermodynamic and chemical limitations of the maximum layer thickness that can be sandwiched between the organic bilayers while retaining the structural integrity of the 2D perovskite.

Novel Low-Dimensional Tin Halide Compounds—Structures, Properties and Perspective Applications

Maksym V. Kovalenko1, 2; 1Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland; 2Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland.

The spatial localization of charge carriers to promote the formation of bound excitons and concomitantly enhance radiative recombination has long been a goal for luminescent semiconductors. Zero-dimensional (0D) materials structurally impose carrier localization and result in the formation of bound Frenkel excitons. We present fully inorganic, perovskite-derived zero-dimensional Sn4+ material Cs8SnBr20 that exhibits room-temperature broad-band photoluminescence centered at 540 nm with a quantum yield (QY) of 10-20 % [1]. A series of analogous compositions following the general formula Cs8n-AnSnBr2n–1 (A=RnB; K; ≤1, ≤1) can be prepared. The emission of these materials ranges from 500 nm to 620 nm with the possibility to compositionally tune the Stokes shift and the self-trapped exciton emission bands.

We also present the synthesis, the structure as well as electronic and optical properties of a family of hybrid tin (II) bromide compounds comprising guanidinium [G, C(NH2)3]+ and mixed cesium-guanidinium cations: G2SnBr6, CSGSnBr6 and Cg2GSnBr6. G2SnBr6 has a one-dimensional structure that consists of chains of corner-shared [SnBr6]2– square pyramids and G cations situated in-between the chains. G2SnBr6 is a luminescent phase with a broad emission band resulting from trapped exciton states. Cs+ exhibits pronounced structure-directing effect: with a mixture of Cs+ and mixed cesium-guanidinium cations: G2SnBr6, CSGSnBr6 and Cg2GSnBr6 compounds. The related strong anisotropies of the halide perovskite lattice distortions have in turn a direct influence on their electronic and optical properties.

References:
2. O. Nazarenko et al. submitted.

Understanding White-Light Emission from Layered Perovskites and Related Materials

Matthew Smith, Adam Jaffe, Aaron Lindenberg and Hemamala Karunadasa; Stanford University, Stanford, California, United States.

In 2014 we observed white-light emission from the inorganic sheets of layered lead-halide perovskites (1). Upon UV excitation, these bulk crystalline solids emit light that spans the entire visible spectrum, similar to sunlight. These hybrid phosphors have high color rendering indices and easily tunable chromaticity coordinates. They are promising as phosphors for solid-state lighting, especially as neat large-area coatings. Recently, a number of other white-light-emitting perovskites and closely related materials have been reported, making this a burgeoning field of study (2). However, the vast majority of layered perovskites display a narrow blue/green emission, and white-light emission remains rare, leading to the question: "what is special about the white-light emitters"?
Over the past several years, we have investigated the generality of obtaining broad photoluminescence from low-dimensional metal-halide lattices. We attributed the white-light emission mechanism to exciton self-trapping, or the trapping of photogenerated electron-hole pairs in transient lattice deformations (1,3), and showed that it is common to all Pb-Br perovskites, although it is highly temperature dependent (4). I will describe our most recent work that provides a more complete picture of the emission mechanism and highlights the generality of exciton self-trapping. Our studies provide design rules for obtaining both the broad white-light emission as well as the narrow blue/green-light emission from these materials. The understanding we have developed of perovskite white-light emitters can be applied to many other low-dimensional systems.

(4) Smith, Jaffe, Dohner, Lindenberg K. Rouznin and Tae-Woo Lee, Science and Engineering, Nanyang Technological University, Singapore, Singapore;

Metal halide perovskites (MHPs) have emerged as a very high promising materials for optoelectronics and photonics, mostly due to their large absorption coefficient and excellent quantum yield of emission at room temperature, among other electro-optical properties of MHPs. The most surprising fact is that these properties are not very different from monocrystalline (or epitaxial films) direct semiconductors, even if MHPs are prepared as polycrystalline thin films by simple deposition methods, as spin-coating, inkjet printing and thermal evaporation, for example. The absorption coefficient is dependent on the material electronic structure and hence mostly intrinsic, but other electro-optical parameters, as the emission quantum yield, will depend on radiative and non-radiative recombination channels for free (and bound) excitons and carriers. In this way, slow carrier recombination in MHPs is considered the origin of the observed large charge carrier diffusion length, whose origin would be the so-called "delayed luminescence" due to the existence of shallow non-quenching traps in these materials [1, 2]. In the talk a revision of recombination dynamics in MHPs will be presented. These materials have been successfully integrated in optical waveguides where stimulated emission is observed with very low thresholds both on rigid and flexible substrates [3-5]. Furthermore, perovskite-based photodetectors can be also integrated in the same platform paving the road towards wearable integrated photonics [5].

Finally, we will present the optical properties of MHP thin films using different organic cations alone or their mixture with methylammonium that produce multi-quantum-well structures (or 2D/3D perovskites). This is an emerging field of work within the scientific community of perovskites, because of the higher efficiency of photovoltaic devices based on these 2D/3D MHPs. Moreover, quantum confinement in these structures introduces a new way to tune the optical properties, especially useful for emitting devices.

REFERENCES


11:30 AM ES17.01.06
Tunable Ferroelectricity in Ruddlesden-Popper Halide Perovskites Qiannan Zhang1, Ankur Solanki1, Mingjie Li2, Davide Giovanni3, Thomas L. Jansen1, Maxim S. Pshenichnikov1 and Tze Chien Sum1,3; 1School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore; 2School of Material Science and Engineering, Nanyang Technological University, Singapore, Singapore; 3Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh, Netherlands.

Ruddlesden-Popper (RP) halide perovskites are promising optoelectronic materials due to their high-performance in PV applications and excellent ambient stability. Their ferroelectric properties provide an exciting opportunity to further improve PV performance based on the nature of their layered structure. Polar domains in ferroelectric materials play an important role in separating electrons and holes. However, the relation between structure and function which lead to the RP ferroelectrics remains unknown. Herein, we realize tunable ferroelectricity in 2-phenylethylammonium (PEA) and methylammonium (MA) RP halide perovskites (PEA)_x(MA)_yPbI_{3x+y}, by varying the number of inorganic layers and tuning the correlation length of the ferroelectric order. Firstly, the non-centrosymmetric nature of RP thin films is confirmed by nonlinear optics. Secondly, switchable polarity leading to ferroelectric properties is validated by piezo force microscopy and polarization-electric field measurements macroscopically and macroscopically. Then, the origin of ferroelectricity in the RP halide perovskites is investigated by MD simulations. Finally, dark current-voltage hysteresis phenomenon implies potential issues for light harvesting and light emitting applications. Importantly, our findings reveal an exciting approach to engineer tunable RP ferroelectrics, which could pave the way to new functionalities for perovskite optoelectronics.

11:45 AM ES17.01.07

In the world of growing energy demand, perovskite materials have emerged as a favorable alternative for next-generation solar cell devices owing to their high power conversion efficiency. The perovskite family is rich in multitudes, and the probability of discovering new and exciting photovoltaic materials are high. To date, most studies on this topic are focused around methyl and ethyl lead iodide structures. Recent advancement in the field of high throughput methodologies have paved a way towards the pursuit of new perovskite complexes beyond the conventional structures, facilitating an understanding of the basic physicochemical properties of these materials. Inverse Temperature Crystallization (ITC) methods were adapted to be compatible with robotic liquid-handler syntheses, resulting in the growth of large single crystals while maintain a high reaction throughput. Chemical spaces were mapped in several related systems and a large reaction dataset was generated for use with machine learning algorithms. A novel approach to prepare and characterize robot-ready perovskite crystals is described for lead halide perovskites.

SESSION ES17.02: High-Performance Light-Emitting Devices
Session Chairs: Barry Rand and Brandon Sutherland
Monday Afternoon, April 22, 2019
PCC North, 100 Level, Room 131 B

1:30 PM ES17.02.01
Highly Efficient Light-Emitting Diodes Based on Lead-Halide Perovskites Young-Hoon Kim1, Himchan Cho1, Min-Ho Park1, Su-Hun Park1, Soyeong Ahn2 and Taeg-Woo Lee2,1; 1Seoul National University, Seoul, Korea (the Republic of); 2Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Lead halide perovskites have been used as emission layers in perovskite light-emitting diodes (PeLEDs), and have many advantages such as high charge-carrier mobility, solution processability, high color purity, color tunability and low material cost. However, low electroluminescence (EL) efficiency of PeLEDs at room temperature is a challenge that must be overcome. Here, we present high-efficiency PeLEDs by controlling the dimension and dimensionality (D) of perovskite grains/crystals to overcome the EL efficiency limitations. First, we kinetically control the grain size in 3D bulk polycrystalline films and achieve uniform methylammonium lead bromide (MAPbBr3) and CsPbBr3 films with...
Efficient and Stable of Perovskite Optoelectronic Devices

Jianpu Wang; Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing, China.

Light-emitting diodes (LEDs), which convert electricity to light, are widely used in modern society—for example, in lighting, flat-panel displays, medical devices and many other situations. Generally, the efficiency of LEDs is limited by nonradiative recombination (whereby charge carriers recombine without releasing photons) and light trapping. In planar LEDs, such as organic LEDs, around 70% to 80% of the light generated from the emitters is trapped in the device, leaving considerable opportunity for improvements in efficiency. Many methods, including the use of diffraction gratings, low-index grids and buckling patterns, have been used to extract the light trapped in LEDs. However, these methods usually involve complicated fabrication processes, and can distort the light-output spectrum and directionality. Here we demonstrate efficient and high-brightness electroluminescence from solution-processed perovskites that spontaneously form submicrometre-scale structures, which can efficiently extract light from the device and retain wavelength- and viewing-angle-independent electroluminescence. These perovskites are formed simply by introducing amino-acid additives into the perovskite precursor solutions. Moreover, the additives can effectively passivate perovskite surface defects and reduce nonradiative recombination. Perovskite LEDs with a peak external quantum efficiency of 20.7% (at a current density of 18 mA cm⁻²) and an energy-conversion efficiency of 12% (at a high current density of 100 mA cm⁻²) can be achieved—values that approach those of the best-performing organic LEDs.

References


Efficient and Stable of Perovskite Optoelectronic Devices

Junbi You; Chinese Academy of Sciences, Beijing, China.

Lead halide perovskites is a new type of semiconductor optoelectronic material, which owns large absorption coefficient, long diffusion length, and also it shows high emission efficiency. This advantages feature it a great potential in in solar cells and also in light-emitting diodes. Recently, there are great breakthrough in these two types of optoelectronic devices, the power conversion efficiency (PCE) and the electroluminescence external quantum efficiency (EQE) have been pushed to 23.3% and over than 20% for perovskite solar cells and light-emitting diodes, respectively. In this talk, I will talk about how we achieve high performance and stable of perovskite based optoelectronic devices according to perovskite film growth control, interface engineering and surface passivation [1-5].

References


Metal halide perovskite generates extremely sharp emission peak and high luminescence quantum yield, enabling it to be a promising candidate as the new generation of emitting materials for displays. However, the development of perovskite LEDs is impeded by their fast carriers diffusion and poor stability in air. Herein, quasi 2D CsPbBr$_3$, quantum wells homogeneously surrounded by inorganic crystalline Cs$_3$Pb$_m$Br$_{3m}$, of large bandgap are grown. The centralization of carriers in nanoregions facilitates radiative recombination and brings much enhanced luminescence quantum yield. The external quantum efficiency and luminescence intensity of the LEDs based on this nanocomposite are one order of magnitude higher than the conventional low dimensional perovskite. Meanwhile, the use of inorganic nanocomposite materials brings much improved device operation lifetime under constant electrical field.

By using bidentate 2,2'-iminodibenzonic acid as conductive ligand, we preprepared CsPbI$_3$ NCs based high efficiency red color light emitting diode. The passivated NCs enabled us to realize red light emitting diodes (LEDs) with 5.02% external quantum efficiency and 748 cd/m$^2$ luminance, which is the highest efficiency realized at that time.

**References**


**4:45 PM ES17.02.08**

**Designing Efficient Energy Funneling Kinetics in Ruddlesden-Popper Perovskites for High Performance Light Emitting Diodes**

**Natalia Yantara, Annalisa Bruno, Azhar Iqbal, Nur Fadilah Jamaludin, Cesare Soci, Subodh Mhaisalkar and Niranjan Mathews; Nanyang Technological University, Singapore, Singapore.**

Ruddlesden Popper (RP) perovskites are of great interest in light emitting diodes (LED), due to the efficient energy transfer (funneling) from high bandgap (donor) domains to low bandgap (acceptor) domains which lead to enhanced photoluminescence (PL) intensity, long PL lifetime, and high efficiency LED. However, the influence of reduced effective emitter centers in the active emissive film as well as the implications of electrical injection into the larger bandgap donor material have been not addressed in the context of an active device. We critically assess and modulate the electrical and optical signatures of the energy cascading mechanisms in a model Ruddlesden Popper perovskite series ((Cs$_x$H$_y$)$_3$Ni$_2$(CH$_3$NH$_2$)$_3$)$_{3m}$Pb$_{3m}$Br$_{3m+1}$). Optimised devices demonstrated a current efficiency of 22.9 cd A$^{-1}$ and 5% external quantum efficiency, more than 5 times higher than systems where funneling was absent. The signature of non-ideal funneling in RP perovskites is revealed by the appearance of donor electroluminescence from the device, followed by a reduction in the LED performance.

**SESSION ES17.03/ES15.01/ES16.03: Joint Session: Halide Perovskites—Celebrating the 10th Anniversary of Perovskite Solar Cell Invention (JACS, 2009, 131, 6050)**

**10:30 AM ES17.03.01/ES15.01.01/ES16.03.01**

**Present Status and Next Important Challenge of Perovskite Photovoltaics Towards Industrialization**

**Tsutomu Miyasaka; Toim University of Yokohama, Yokohama, Japan.**

Power conversion efficiency (PCE) of lead halide perovskite solar cell (over 23%) has surpassed those of CIGS and CdTe, approaching the top value of crystalline Si cell. Our group has been able to achieve PCE over 21% by low cost ambient fabrication. However, high PCE of single-cell enabled by lead halide-based perovskite absorbers are now being saturated, taking the Shockley Queisser (SQ) limit of open-circuit voltage ($V_{OC}$ ca.1.32V) into account. Tandem cell making, which can further increases PCE up to 28% or more, leads to higher material and process cost and will raise a question if performance/cost ratio can be accepted in industry. Therefore, a smart way is to create a single cell which has high PCE comparable with that of GaAs (>28%) by reducing bandgap energy to <1.4 eV without accompaniment of increase in $V_{OC}$. This possibility will be in a family of metal halide perovskite out of those depending on use of lead. In addition to such efficiency issue, high performance of organo lead halide materials is not compatible with robust high stability required for practical use. Ensuring the intrinsic thermal stability (desirably >200°C) of the perovskites is a key issue before industrialization. In addition, toxicity of lead-based perovskites are going to become the most formidable challenges for real use (commercialization), in particular, for applications to IoT society, which is one of the most promising field of perovskite photovoltaic device in terms of high voltage output even under weak illumination. These thoughts urge us to concentrate our next research of perovskite photovoltaics (PV) more on development of non-lead high efficiency absorbers. Sn perovskite is still a strong candidate because Sn(II) has been found to be stabilized against ambient air by metal doping method (such as Ge). Regarding Bi-based perovskites, we found AgBiI$_3$ as a promising all-inorganic absorber having high thermal and moisture stability. Stability also highly depends on the property of charge transport materials (CTMs), especially, the kind of hole transporter. Spiro-OMeTAD does not work at high temperature while P3HT, for example, is thermally stable. In our collaboration with JAXA, P3HT-based perovskite devices showed robust stability by exposure to high (100°C) and low (<80°C) temperature and also to high energy particle radiations (Science, 2018, 2, 148). Selection of CTMs is another important key in combination with non-lead perovskite materials. In conclusion, next direction of perovskite PV should be to enhance PV performance of non-lead all-inorganic semiconductor materials by extended compositional engineering, in parallel with developing thermally stable CTMs. Our on-going studies on non-lead perovskite materials in our group will be introduced in the talk.

**11:00 AM ES17.03.02/ES15.01.02/ES16.03.02**

**Issues and Solutions in Perovskite Solar Cells**

**Nam-Gyu Park; Sungkyunkwan University, Suwon, Korea (the Republic of).**

Since the first report on the high efficiency, stable perovskite solar cell (PSC) in 2012 by our group, following two seed works on perovskite-sensitized liquid junction solar cells in 2009 and 2011, PSC demonstrated its power conversion efficiency (PCE) of 23.3% in 2018. According to Web of Science, publications on PSC increase exponentially since 2012 and total number of publications reaches already over 10,000 as of October 2018, which is indicative of a paradigm shift in photovoltaics. Although small area cell exhibited superb efficiency surpassing the performance of thin film technologies, scale-up technology is required toward commercialization. In addition, further higher efficiency toward Shockley–Queisser limit is required in parallel. In this talk, Large-area coating technology is introduced using perovskite cluster embedded coating solution, followed by brief introduction on history of perovskite solar cell. Bi-facial stamping method was developed for not only scale-up technique but also interface modification and low-temperature phase stabilization. For higher efficiency, managing recombination is critical. Methodology reducing recombination is developed via interface and bulk engineering. Current-voltage hysteresis is also discussed because hysteresis is related to the stability of perovskite solar cell. Ion migration is now visualized and confirmed to correlate with hysteresis.

**11:30 AM ES17.03.03/ES15.01.03/ES16.03.03**

**Hybrid Halide Perovskite Semiconductors—An Historical Perspective**

**David B. Mitzi; Duke University, Durham, North Carolina, United States.**

Organic-inorganic perovskites enable a combination of useful organic and inorganic properties within a single molecular-scale composite and have attracted substantial interest for use within organic-inorganic electronic devices [1], in part due to the high carrier mobilities, long minority carrier lifetimes, tunable band gaps and relatively benign defects and grain boundaries for systems based on Group 14 metals (e.g., Ge, Sn and Pb) [2]. Indeed, these materials have enabled unprecedented rapid improvement in perovskite photovoltaic performance to levels above 20% power conversion efficiency and with open circuit voltages above 1V for a single junction photovoltaic (PV) device [3]. This talk will provide an historical perspective on foundational work related to the organic-inorganic perovskite semiconductors, including discussion of crystal structure flexibility [4,5], semiconducting properties, film deposition approaches and electronic device applications of the three-dimensional and lower-dimensional perovskite structures. Recent trends in the field, as they relate to application in photovoltaics and related devices, will also be coupled into this discussion.
The contribution is concerned with the significance of ionic conduction for hybrid perovskites. It starts with outlining the analysis of the nature of the ionic charge carriers and the quantification of their contributions to the overall transport in methyl-ammonium lead iodide. Apart from NMR, tracer exchange and doping experiments, detailed electrochemical experiments form the basis of these investigations. The prevailing mobile carriers are iodine vacancies, holes and conduction electrons. The analysis also reveals the adjusting screws that can be used to tune the charge carrier chemistry – mostly component partial pressure (iodine activity) and doping content [1-3].

The consequence of the mixed conductivity is not only carrier and mass transport, as it is decisive for chemical kinetics (e.g. decomposition kinetics), but also the occurrence of a substantial chemical capacitance [1,4]. These phenomena are well understood for oxide perovskites the behavior of which is analogous to the situation in the hybrid perovskites under dark conditions. Of particular relevance is the occurrence of a distinct long-time polarization (also the hysteresis in CV experiments) which is not a dielectric or space charge polarization, but a true bulk phenomenon. This stoichiometric effect is known as Wagner-Hebb polarization and is one of the basic phenomena in Solid State Ions involved e.g. in resistance degradation or electro-coloration.

A special role is played by oxygen because depending on the time window, its influence leads either to a varied iodine potential, to a doping effect or to a global decomposition. The understanding of this complex behavior reflects our far-reaching defect-chemical understanding of methyl-ammonium lead iodide [5].

In addition to understanding and influencing ionic and electronic carrier concentrations by classic Solid State Ionics principles, we also applied strategies of Nanoionics (e.g. heterogogeneous doping) [6]. In addition to offering further degrees of freedom for charge carrier tuning, such research reveals new insight into the interface chemistry, such as ionically dominated space charge zones. Most recent results are presented [7].

Last but not least, the striking finding of an enormously light-enhanced ion conductivity will be addressed. This is – also from the viewpoint of Solid State Ions – completely unexpected. The reason for this phenomenon is presented and implications for photo-decomposition but also for the design of novel “opto-ionic” devices are discussed [8].

References

Organic-inorganic hybrid perovskites (OIHs) have attracted extensive interest for potential use in next-generation photovoltaic devices due to the demonstrated high power conversion efficiency, low materials cost, and low fabrication cost. For conventional inorganic perovskites, commercial applications mainly rely on the strong electromechanical coupling, including both piezoelectricity and electrostriction. OIHs materials possess a similar lattice structure as conventional inorganic perovskites, however, the electromechanical coupling of OIHs has barely been explored. Here, we report the electrostrictive response of the MAPbI3 hybrid perovskite crystals as large as 1% compressive strain under a field of 3.7 V/μm along the electric field direction with a corresponding to an electrostrictive coefficient of ~730 nm/V2 and mechanical energy density of 0.74 J/cm2. Superior to other electrostrictive materials, MAPbI3 demonstrates both large electrostrictive strain and large elastic energy densities under a small applied field. The electrostrictive strain is independent of the electric field polarity and has a quadratic dependence on the electric field. The electrostrictive response time is in the order of millisecond. The influences of piezoelectricity, thermal expansion, intrinsic electrostrictive effect, Maxwell stress, ferroelectricity, local polar fluctuation, and methylammonium cation ordering on this electromechanical response are excluded. We speculate, using density functional theory, that electrostriction of MAPbI3 likely originates from lattice deformation due to the formation of additional defects under applied bias. Since almost every electronic device either operates under applied electric field or experiences an internal built-in field which is close to the field of 3.7 V/μm inducing 1% strain, the discovery of electrostriction and its origin may also impact the design and performance of OIH-based electronic devices, including solar cells, LEDs, photodetectors, and radiation detectors. The discovery of large electrostriction in lead-iodide perovskites may lead to new potential applications in actuators, sonar, and micro-electromechanical systems, and aid the understanding of other field-dependent material properties.

Suppressed Phase Separation in Mixed-Halide Perovskites

Xi Wang1, Yichuan Ling1, Yan Xin1, Kamal Dhungana2, Fernando Perez-Orive1, Xiujun Lian1, Navon Knox1, Zhizhong Chen1, Yan Zhou1, Drake Beery2, Kenneth Hanson3,4, Jian Shi3, Shanglei Lin2,5 and Hanwei Gao1,6,7

Florida State University, Tallahassee, Florida, United States; 2Condensed Matter Science, National High Magnetic Field Laboratory, Tallahassee, Florida, United States; 3Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, United States; 4Mechanical Engineering, Florida State University, Tallahassee, Florida, United States; 5Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; 6Condensed Matter Science, National High Magnetic Field Laboratory, Tallahassee, Florida, United States; 7Materials Science & Engineering Program, Florida State University, Tallahassee, Florida, United States.

Mixing different halogen ions provided a convenient means to tune the bandgaps of halide perovskites (e.g. CsPb(BrI)1-x). The so-called mixed-halide perovskites, however, suffered from severe phase separation under optical illumination. In this talk, we will present a facile approach to suppress such phase separation by making the mixed halide
perovskites into composites. The tuned bandgap remained remarkably stable even under optical illumination 440 W/cm²at 405-nm (The AM1.5 spectrum has an integrated power of 0.1 W/cm²). The mechanism responsible for the suppression of phase separation pointed to a model based on thermodynamic nucleation, which was further verified by the temperature dependent photoluminescence. The tuned and stabilized bandgap is expected to be essential for the development of perovskite-based optoelectronics, such as tandem or concentrated solar cells, full-color LED displays, or wavelength-specific photodetectors.

3:00 PM BREAK

3:30 PM *ES17.04.05

The perovskite crystal structure hosts a wealth of intriguing properties, and the renaissance of interest in halide (and hybrid organic-inorganic) perovskites (HOIPs) has further broadened the palette of exciting physical phenomena. HOIPs have recently received great attention as candidates for commercially viable and efficient conversion of solar energy. Breakthroughs in HOIP synthesis, characterization, and solar cell design have led to remarkable increases in reported photovoltaic efficiency. However, the observed long carrier lifetime and PV performance have eluded comprehensive physical justification, and the performance and stability of these materials is greatly affected by water and moisture in the environment.

In this talk, recent theoretical progress in understanding HOIPs will be reviewed and integrated with experimental findings, and we investigate the nature of water interactions in hybrid perovskite MAPbI₃. By varying water concentration over two orders of magnitude, we study the process of water infiltration and the surface and bulk chemistry that follows and leads to first reversible, and then irreversible changes to the material’s structure. We discuss, based on electronicstructure analyses, how water changes the optical properties of the material in different concentrations. In addition, the large amplitude motions of HOIPs will be highlighted, including ionic diffusion, anharmonic phonons, and dynamic incipient order on various length and time scales. The intricate relationships between correlated structural fluctuations, polar order, and excited charge carrier dynamics will also be discussed.

This understanding of the nature of water-HOIP interactions and ionic dynamics should lead to the design of better and more stable solar cells.

4:00 PM *ES17.04.06
Impact of Bias-Induced Ion Migration in Perovskite-Based Light-Emitting Diodes Trung-Fang Guo¹,², Teng Lam Shen¹, Nan-Jay Chiou¹, Chun-Hua Shih¹, Jeng-Jun Chen¹, Ying-Chi Chen¹ and Loganathan Aswaghosh¹; ¹Department of Photonics, National Cheng Kung University, Tainan, Taiwan; ²Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan, Taiwan.

The electroluminescence (EL) intensity as well as the efficiency are usually low for perovskite-based light-emitting diodes (PeLEDs) biased at the low current density regime, but markedly raise to a maximal magnitude at the high voltage or current biasconditions. We observe a nonlinear EL intensity versus current density curve (L-I curve) of devices and attribute this observation to the bias-induced migration of ions in perovskite active layer (CH₃NH₃PbBr₃) to modulate the device performance. In this work, we utilize the ac impedance and photoluminescence (PL) spectroscopy to characterize the effect of ion migration in polycrystalline CH₃NH₃PbBr₃ layer. The passivation of ionic defects by the mobile ions as induced by the electric bias markedly enhances PL magnitude of the polycrystalline CH₃NH₃PbBr₃ layer in PeLEDs. Here, by adding a small amount of additives to the polycrystalline CH₃NH₃PbBr₃ layer possibly passivates the surface ionic defects and suppress the inter-grain ion migration. We find a decrease of ionic conductivity in perovskite active layer by the additives in impedance measurement. In addition, as characterized by SEM, XRD, and PL measurement, adding the additives reduces the average crystalline size, enhances PL intensity, and elongates the carrier lifetime, but did not change the basic crystal structure of CH₃NH₃PbBr₃ perovskite. We observe the linear correlations of L-J curve for devices biased at different current regimes and the markedly enhanced brightness and efficiency of PeLEDs at the low current regime to be the feature of a decent LED.

4:30 PM ES17.04.07
Roles of Solvate Complexes in the Kinetics and Reversibility of Light-Induced Phase Separation Rhiannon (Rhys) M. Kennard, Clayton J. Dahlman, Ryan A. DeCrescent, Jon Schuller, Ram Seshadri and Michael L. Chabinyc; University of California, Santa Barbara, Santa Barbara, California, United States.

Halo perovskite nanocrystals exhibit exceptional brightness in vivid colors and with narrow emission bandwidths, making these materials potential “game-changers” for display technologies and light-emitting devices more generally. Bandgap tunability over the entire visible spectrum can be easily accomplished via halide mixing, with mixed chloride-bromide perovskites emitting in the blue-green range and mixed bromide-iodide perovskites emitting in the green-red range. However, at sufficiently high excitation intensities or in larger-dimension mixed-halide perovskites, light exposure causes phase separation of bromide-iodide perovskites into Br-rich and I-rich regions, limiting the applicability of these materials. Because the I-rich regions formed have narrower bandgap than the Br-rich regions, charges become trapped in the I-rich regions, which limits carrier mobility and causes large anomalous red photoluminescence. Strategies to suppress this light-induced phase separation (LIPS) have involved reducing perovskite crystal size or filling halide vacancies. However, much still remains unknown regarding LIPS – in particular, the potential roles played by solvent complexes/ perovskite intermediates in enhancing or mitigating LIPS has not been explored. This talk will discuss the contributions of solvent complexes to the kinetics and reversibility of LIPS in methylammonium lead bromide-iodide thin films, and will illustrate LIPS mechanistic pathways that are not tied to solvates. The insights gained by this study are expected to aid future design of LIPS-free mixed-halide perovskite devices.

LIPS is characterized by an intense red photoluminescence signal near 1.7 eV that grows with time as the I-rich phase forms, combined with a reduction in emission from the original bandgap of the mixed-halide perovskite. The rate of red photoluminescence (red-PL) growth increased strongly when large amounts of solvent remained in the film, suggesting a dynamic process in which solvent complexes aid formation of I-rich phases under light exposure. Correspondingly, in harshly-annealed films, longer exposure times were needed to induce LIPS. LIPS occurred more slowly in Br-rich films than in I-rich films (all harshly-annealed), suggesting that defect accumulation near iodide is necessary to induce LIPS. In harshly-annealed films, LIPS red-emission spectra exhibited multiple previously-unreported emissive states, which was attributed to formation of intermediary I-rich and Br-rich phases before formation of the equilibrium I-rich and Br-rich phases. Finally, solvent complexes enhanced red-PL growth reversibility, as evidenced by greater reversibility in unannealed films. These results provide guidelines for synthesizing solvate-free mixed-halide perovskite films and potentially identify novel LIPS kinetic pathways. We anticipate that the insights gained by this study will aid in understanding LIPS and design of LIPS-free mixed-halide perovskite optoelectronic devices.

SESSION ES17.05: Poster Session
Session Chair: Yuanyuan Zhou
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES17.05.01
Insight into the Role of Ligands in Halide Perovskite Nanocrystal Synthesis and Tuning the Perovskite Structure, Shape and Size of the CsPbBr₃ Nanocrystal Youngtaek Yoo and Soo Young Kim; Chung-Ang University, Seoul, Korea (the Republic of).

Colloidal nanocrystals of inorganic cesium lead halide (CsPbX₃, X = Cl, Br, I, or combinations thereof) perovskites have attracted much attention for photonic and optoelectronic applications due to the high carrier mobility, easily tunable optical absorption range, manufacturing simplicity and low cost. The optical and electrical properties of the halide perovskites significantly depend on their crystal structure, shape and size. And there were many studies on the shape and size of perovskite nanocrystals related to reaction time,
reaction temperature, and ligand changes. However, the roles of the acid ligand and the amine ligand were not identified.

In this study, we are able to control the shape and size of CsPbBr$_2$ perovskite nanocrystals by using different kinds of the ligands and changing the concentration of the ligands. By observing these phenomena, we could understand the respective effects of acid ligand and amine ligand on the structure, shape and size of perovskite nanocrystals. The acid ligands influenced the structure and shape of the perovskite nanocrystals. With acetic acid ligand, the 2D perovskite structure CsPbBr$_2$ nanorods were synthesized through the facile ligand-mediated synthesis. The 3D perovskite structure CsPb$_{2}$Br$_5$ nanosheets were synthesized using other acid ligands. And small nanorods and nanospheres were mixed in some cases. The amine ligands had a large effect on the size of the perovskite nanocrystals. The size of the nanocrystals decreased as the amine ligand became longer, and the crystal size could be finely controlled by adjusting the amount of the amine ligand. We believe that our report helps to understand the synthesis of halide perovskite for the application in optoelectronic devices.

ES17.05.02
Unprecedented White-light Emission from the Deep Trap States of Two-Dimensional Perovskites ($\text{Cs}_x\text{CH}_3\text{NH}_3\text{PbBr}_3\text{Cl}_4$) for the Light-Emitting Diodes Mi Hee Jung; Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul, Korea (the Republic of).

Two-dimensional (2D) perovskite, which consists of inorganic layers bearing electronic functionality and organic layers that act as a template for the structure, has attracted a lot of attention due to their superior stable optoelectronic properties. Especially, one of the emerging applications for 2D perovskite is broadband white-light emission for solid state lighting. With the help of the facile one-step synthesis, the 2D perovskite structure CsPbBr$_2$ nanoparticles were synthesized using the mixture of different ligands. And small nanorods and nanospheres were mixed in some cases. The amine ligands had a large effect on the size of the perovskite nanocrystals. The size of the nanocrystals decreased as the amine ligand became longer, and the crystal size could be finely controlled by adjusting the amount of the amine ligand. We believe that our report helps to understand the synthesis of halide perovskite for the application in optoelectronic devices.

ES17.05.03
Synthesis of Core/Shell Perovskite Nanocrystal for Fabrication Wide-Color-Gamut LCDs Hyeongjin Lee, Hee Chang Yoon and Young Rag Do; Kookmin University, Seoul, Korea (the Republic of).

In this study, green (G) CsPbBr$_2$/CsPbBr$_3$ and red (R) CsPbBr$_{3.3}$-I$_{0.7}$/CsPbBr$_4$ core/shell perovskite nanocrystals (PeNCs) are synthesized and utilized for the development of highly efficient and wide-color-gamut PeNC-emissive liquid crystal displays (LCDs). The photoluminescence quantum yields (PLQYs) for G and R core/shell PeNCs reached 77.4% and ~78.9%, respectively. The improved photo-stability and water resistance of the GR PeNC films imply more opportunities to fabricate GR color-converting films with these materials to replace GR color filters (CFs) in conventional LCDs. The realization of color-by-blue PeNC emissive-LCDs can overcome technical challenges related to conventional CF-assisted LCDs through the realization of introducing improved device efficiency levels and an enlarged color gamut. The conversion efficiency rates of a color-by-blue core/shell PeNC-emissive LCD consisting of G and R PeNC films sandwiched in the form of a recycling bottom layer and a blue-filtering top dichroic filter are 42.0% and 44.3%, respectively. The color gamut was enlarged to 134% compared to the NTSC standard. The GR colloidal PeNCs and the fabricated PeNC-films were analyzed by TEM, XRD, and EDX in terms of their structural properties, and by PL and EL with an integrating sphere with regard to their optical properties. This color-by-blue PeNC-emissive LCD represents an excellent opportunity to create new emissive-LCD products to replace traditional RGB CF-assisted LCDs.

ES17.05.04
Development of Novel and Highly Stable Crystals of Lead-Free Double Perovskite Based-on Bismuth Tineh Ma and Chu Zhang; Kyushu Institute of Technology, Kitakyushu, China.

Recently, bismuth-based perovskites have aroused as a promising choice in replacing the lead-based perovskites due to its non-toxic and stable 6p-block structure properties. In addition, computational predictions suggest that Bi-based perovskite exhibits lower intrinsic trap densities and defect states, long carrier lifetime and its defect-tolerate properties which the lead-based perovskite nanocrystals (PeNCs) and lead-free double perovskite via one-step facile hydrothermal process. In this work, we provided an in-depth study on the CNBI crystal growth process under the influence of various acid concentrations and its plausible crystal growing mechanisms. We here present our work on the succession in synthesizing high crystallinity, stable, and novel Cs$_x$Na$_{3-x}$Bi$_2$I$_{6-x}$ lead-free double perovskite via one-step facile hydrothermal process. By using different kinds of the ligands and changing the concentration of the ligands. By observing these phenomena, we could understand the respective effects of acid ligand and amine ligand on the structure, shape and size of perovskite nanocrystals. The acid ligands influenced the structure and shape of the perovskite nanocrystals. With acetic acid ligand, the 2D perovskite structure CsPbBr$_2$ nanorods were synthesized through the facile ligand-mediated synthesis. The 3D perovskite structure CsPb$_2$Br$_5$ nanosheets were synthesized using other acid ligands. And small nanorods and nanospheres were mixed in some cases. The amine ligands had a large effect on the size of the perovskite nanocrystals. The size of the nanocrystals decreased as the amine ligand became longer, and the crystal size could be finely controlled by adjusting the amount of the amine ligand. We believe that our report helps to understand the synthesis of halide perovskite for the application in optoelectronic devices.

ES17.05.05
Blue-Emissive CsPbBr$_5$ Quantum Dots in a Gel Matrix Marta Valles-Pelarda, Carles Felip-León, César A. Angulo-Pachón, Juan F. Miravit, Francisco Galindo and Ivan Mora-Sero; University of Jaume I, Castellón, Spain.

Metal halide perovskite nanocrystals have been deeply studied in the last years due to their multiple properties and applications. These materials usually have a high photoluminescence quantum yield (PLQY), narrow emission bandwidth and their band-gap is tuned easily by changing the chemical composition of the nanocrystals or by varying their morphology from cubic structures to nanoplatelets. All these outstanding properties make them suitable for optoelectronic applications, sensors and lasers. For the entire visible range, emissive perovskite nanoplatelets have been achieved. However, high PLQY blue emissive nanoplatelets are still a challenge, with high chloride content having relatively low PLQY. Recently, 70% was reported for CsPb$_2$Br$_5$ nanoplatelets and in films 88%, obtained with a mixture of different perovskites. [1,2] In this work, a combination of CsPb$_5$Br$_9$ nanoplatelets and a gelator agent leads to a blue-emissive gel, with PLQY of ~70% which is a high value compared with the PLQY of the nanoplatelets themselves (~75%). Interestingly, depending on the structure of the gelator agent, different behaviors are observed, tuning the emission. In addition, they present a great stability in ambient conditions, after 4 months the PLQY decreased only 7%. The nanoplatelets and the gel with nanoplatelets were also characterized by TEM. [1] B. J. Bohn, Y. Tong, M. Gramlich, M. L. Lai, D. Doblinger, K. Wang, R. L. Z. Hoye, P. Muller-Buschbaum, S. D. Stranks, A. S. Urban, L. Polavarapu and J. Feldmann, Nano Letters, 2018, 18, 5231-5238.


ES17.05.06
Photoluminescence Properties of Ba(Mg$_{0.5}$Nd$_{0.5}$)$_2$O$_4$:Eu$^{3+}$ Red-Emitting Phosphor with High Color Purity Jie Shen, Zixing Wang, Jing Zhou and Wen Chen; Wuhan University of Technology, Wuhan, China.

Phosphor-based white light-emitting diodes (WLEDs) have become a kind of attractive solid light source due to their merits of being environmentally friendly and exhibiting energy savings, high brightness, high luminous efficiency and a long lifetime [1]. The white LEDs based on the near-UV (NUV) light chip and red/green/blue (RGB) primary phosphors have been widely studied for their tunable color rendering index and color temperature [2]. However, the red phosphors which can be excited by NUV light in the
range of 380-410 nm are facing challenges such as their low efficiency, instability and lack of red-color purity, resulting in low color rendering index and high color temperature of white light [3]. Therefore, it is of paramount importance to find a desirable red-emitting phosphor, with good thermal stability and strong luminescent intensity, which can be successfully excited by the NUV light.

In this work, Ba(Mg1/3Nb2/3)O3 was employed as a host of the phosphor with the considering of its low phonon energy [4] and good optical properties [5], and a new red phosphor, Eu3+ ions doped Ba(Mg1/3Nb2/3)O3 was prepared by wet chemical method. Structure characterization results show that all the BMN:Eu phosphors, with various doping contents, have long-range ordering hexagonal perovskite structures and Eu3+ ions replace Ba2+ ions occupying at 2d sites with C2v point symmetry in BMN. The phosphors exhibit the apparent absorption located at 395 nm which matches well with the emission of NUV LED chip, and show the bright red emission of D1s-F2 transitions under the excitation of 395 nm NUV light. The Commission Internationale de L’Eclairage (CIE) chromaticity coordinate (0.657,0.343) of BMN:5%Eu phosphor is close to the standard value (0.670, 0.330) of red phosphors, which indicates that BMN:Eu is a promising red-emitting phosphor for NUV-based WLEDs.

References:

ES17.05.07
Yellow Emissive Near Ultraviolet Light-Emitting Diodes Using MAPbBr3 Perovskite as a Phosphor Seonghoon Jeong, Munisk Oh and Hyunsoo Kim; School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju-si, Korea (the Republic of).

Recently, inorganic III-nitride compound semiconductors have been applied in various fields. In particular, light-emitting diodes (LEDs) are being used in a lot of lighting applications with long-term stability, high efficiency and the field of their use is expanding. The GaN-based LEDs has advantages of high efficiency and light emission of various wavelengths by the composition of In and Al. However, a high level of epitaxial growth technology is required, and it is difficult to form Ohmic electrodes according to the compositional change. To emit white light, a blue LEDs chip and encapsulated phosphors to emit yellow light and mixed with blue light. However, the emitted light reduces the conversion efficiency of 50–80% caused by Stokes loss.

Conventional inorganic white LEDs suffer not only loss of conversion efficiency but also heat generation and possible package deterioration. There have been many studies in many groups to overcome this problem. However, the efficiency of white LEDs using phosphor is not remarkable. Recently, optical device research using halide perovskites has been reported. Perovskite is a semiconductor material structure with cubic AMX3 (A, M cation, X anion) composed of metal and halogen elements. It can control the emission spectrum by changing the element. Metal halide perovskite has been extensively studied as an active layer of solar cells and optical devices. Perovskite has advantages such as high carrier mobility, wavelength change due to halogen element composition, simplicity of process and low cost, so that it is competitive as a photoelectric material. However, it has a drawback that it is very vulnerable to oxygen and moisture, and research is underway to improve it. Many studies have used the high absorbance of perovskite as an active layer. However, we did not use it as an active layer but as a phosphor to convert light emitted from UVLEDs.

In this study, we synthesized perovskite and studied the fabrication method of LEDs which emits yellow light by using synthesized perovskite with UVLEDs phosphor. The synthesized MAPbBr3 was confirmed to have a wavelength peak of 539 nm using the photoluminescence (PL). The Br-containing perovskite was coated under the substrate of the fabricated UVLEDs and the electroluminescence (EL) spectrum was analyzed using a probe-station system equipped. The wavelengths of typical UVLEDs were observed 365 nm main peak wavelength and deep-level wavelength in the range of 500-600 nm. In contrast, UVLEDs coated with perovskite exhibit a stronger light emission at 539 nm with a wavelength of 365 nm and a distinct difference is observed through the emission image. The wavelength of the emitted UV region emitted from the UVLEDs emitted light at 539 nm due to absorption in the coated perovskite. Since the emission spectrum of perovskite is easily adjustable, our novel method will be a new avenue for white LEDs using perovskite instead of conventional phosphors.

ES17.05.08
New Cross-Linkable Hole Transporting Materials for Perovskite LEDs Seokwoo Kang1, Seonwoo Park1, Tae Wan Kim2 and Jongwook Park1; 1Chemical Engineering, Kyung Hee University, Suwon, Korea (the Republic of); 2Physics, Hongik University, Seoul, Korea (the Republic of).

In conventional organic light emitting diode (OLED) as well as perovskite light emitting diode (pLED) device, polyvinyl carbazole (PVK) and Poly-TPD have been widely used as a hole transporting layer (HTL) in the past. However, PVK and Poly-TPD have disadvantage in terms of soluble property limitation during stacked-soluble process device preparation. Therefore, we synthesized new cross-linkable HTL polymer, SMFP-DNBp for pLED device. It has non-soluble property to general solvent after thermal treatment and curing process. It includes phenyl naphthyl group, spirofluorene, and vinyl group. The device configuration is ITO/PEDOT:PSS-PSS:Na/ SMPF-DNPB or others/2D perovskite/TOPO/TBb/LiF/Al. When new HTL materials were used, it showed high luminance efficiency of more than 10 Cd/A in green pLED device.

ES17.05.09
Low Temperature Photoluminescence Mapping of Solar Cells Andrew J. Baker1, 2, Steve Johnston2 and Dana Sulas2; 1Clairmont University, Freedom, Pennsylvania, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.

Photoluminescence mapping provides spatial information about a semiconductor’s (photovoltaic’s) defects, efficiency, bandgap, uniformity, and other important properties. Near liquid helium temperatures, photoluminescence peaks in the spectra become sharper than those observed at higher temperatures, and transitions not resolved at room temperature become observable. An automation system was designed to collect low temperature photoluminescence maps of solar cells to exploit the extra information obtained from cooling the sample being mapped. The photoluminescence spectra were collected from the sample at different temperatures by inserting the sample in a helium-based closed-cycle cryostat.

Automation was developed in which a LabView application controls the low temperature PL mapping process. This involved controlling the following mapping components: motion stages to scan the incoming light source and optics, the temperature of the cryostat, and the PL data collection via a spectrometer/camera combination. The result of combining these components was a system that generates PL maps at temperatures as low as ~8 K. A spatial filter was added to the system to remove signal generated from anywhere other than the point of interest. This addition helped the system approach the theoretical resolution achievable. The completed prototype will be used to study degradation of perovskite solar cells among other types of solar cells.

ES17.05.10
Functionalized Grain Boundaries in Halide Perovskite Materials and Devices Yuanyuan Zhou; Brown University, Providence, Rhode Island, United States.

Grain boundaries (GBs) are the most prominent microstructural features that play significant roles in determining the chemical and physical properties of halide perovskite (HP) thin films. Herein, we demonstrate the concept of ‘GB functionalization’ to manipulate the GB structures in a rational way. The detailed microstructures of functionalized GBs are carefully characterized, which are co-related to the enhanced properties and optoelectronic performance. In addition, the formation mechanisms of these functionalized GBs in HPIs are elucidated.

ES17.05.11
Efficient and Stable Ti- and Sn-Based Lead-Free Perovskite Solar Cells Min Chen1, Minggang Ju2, Xiao C. Zeng2, Yuanyuan Zhou1 and Nitin P. Padture1; 1Brown University, Providence, Rhode Island, United States; 2University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

The state-of-the-art high efficiency perovskite solar cells (PSCs) contain lead and organic cations in the perovskite light-absorber. However, the toxicity associated with the lead and the volatility of the organic cations are hurdles in the path towards the future commercialization of PSCs. While there has been effort towards replacing lead cation with less toxic cations, typical lead-free PSCs still suffer from the low power-conversion efficiency (PCE) and poor stability. Herein, we were firstly inspired by calculation results from Ti-
Based robust double perovskite materials and then realized the PCE (> 3%) on such materials. Meanwhile, we utilized an alloying strategy in all-inorganic Sn-based perovskite materials and realized those PSCs with a promising PCE (> 7%). Furthermore, the formation native-oxide layer passivation effect resulted in superior air-stability for these perovskite materials. Thus, this work provides a new avenue for the design and development of high performance and stable Lead-free PSCs.

ES17.05.12
Extra-Large Grain Formation in Formamidinium Lead Iodide Perovskite Thin Films and Observation of Special Sub-Grain Boundaries Srinivas K. Yadavalli, Wenhai Li, Yuanyuan Zhou, Rashid Zia and Nitin P. Padture; Brown University, Providence, India.

Formamidinium Lead Iodide (FAPI) based perovskites have achieved a great deal of interest as solar cell absorbers due to their superior thermal stability and more suitable band gap compared to methylammonium based perovskites. Here, we report a new phenomenon, where fine-grained (~175 nm)-FAPII thin films transform rapidly to phase-pure n-FAPII. OHII thin films with ultra large grain size exceeding an unprecedented ∼5μm. The large grain nature of the films is confirmed using appropriate materials characterization. 

The improved kinetics of transformation is explained by studying the phase and morphological evolutions during film-solvent interaction. The nature of phase nucleation and growth is studied through in-situ microscopy techniques. In-situ X-ray diffraction and solvent polarity effect on the transformation rate also are studied to corroborate the proposed mechanism. Photoluminescence microscopy was carried out to probe into carrier diffusion within grains and grain boundaries. Eventually, the entire grain gives identical EBSD signal, it was observed that there exist sub-grain boundaries which obstruct carrier diffusion within the grains and likely limit the electronic properties. The passivation or tampering of sub-grain boundaries can become critical in improving the optoelectronic properties and hence need to be investigated further.

ES17.05.13
Magnetic Ordering of a Perovskite-Like La-, Nd-, and Gd-Doped Bismuth Ferrite Valery Sobol1, Barys Korzun2, Olga Mazurenko1, Temirkhan Bzhigistov4 and Sabit Tomaev4, Belarusian State Pedagogical University, Minsk, Belarus; 1The City University of New York, BMCC, New York, New York, United States; 2Belarusian Republican Foundation for Fundamental Research, Minsk, Belarus; 3Taraz State Pedagogical University, Taraz, Kazakhstan.

Bismuth ferrite (BiFeO3) is promising as magneto-electric material because both ferroelectric and antiferromagnetic orders coexist in this material at room temperature. Doping of BiFeO3 or the substitution of bismuth by other chemical elements can modify its magnetic properties. The goal of this paper is to determine the influence of bismuth substitution by rare earth elements La, Nd, and Gd on magnetic ordering in bismuth ferrite.

Substitutional alloys of BiFeO3 of the types Bi1-xLaxFeO3, Bi1-xNdxFeO3, and Bi1-xGdxFeO3 were synthesized by solid-state reaction method using powders of Bi2O3, Nd2O3, Gd2O3, La2O3, and Fe2O3 oxides of pure grade quality. The X-ray diffraction method was applied using the diffractometer Dron-3 on Cu Kα radiation to control crystal structure. Experimental data were collected during scanning, which was repeated ten times in the 2θ range from 20° to 90° at the scanning speed of 10°/6 min. The magnetization was measured using an automated vibrating sample magnetometer (VSM, Oxford instruments) in magnetic fields up to 1 T. Temperature measurements were carried out using Physical Property Measurement System equipped with a 9 T superconducting magnet (PPMS: Model 6000, Quantum design).

It was found that undoped samples of bismuth ferrite BiFeO3 show typical temperature dependence of magnetization, namely the jump of magnetization at 640 K and a lowering of ferromagnetic ordering—below this temperature. Total substitution of 0.10 - 0.15 atomic part of Bi by La, Nd, and Gd leads to the paramagnetic behavior of the doped bismuth ferrite at low temperatures in a wide range of magnetic field. Strong nonlinear dependence of magnetization on the magnetic field at low temperatures was detected. A ferromagnetic-like dependence of magnetization was observed for small magnetic fields. It can be explained by the exchange interaction between doping magnetic ions, as well as by the exchange interaction of these ions with ions of iron. It can be concluded that it is possible to change the initial magnetic ordering of bismuth ferrite by its doping by rare earth elements for the concentrations smaller than 0.10 atomic part of the doping element.

ES17.05.14
Low-Dimensional Lead-Free Halide Perovskites with Functional Organic Spacers Minggang Ju and Xiao C. Zeng; Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, United States.

Low-dimensional organic-inorganic halide perovskites (OIHs) have been hot topic lately for solar-cell applications, largely owing to their markedly high chemical stability. However, most low-dimensional OIHs show much lower device performance than their 3D counterparts, due mainly to the strong quantum-confinement and dielectric effects. Both properties are highly dependent on the “inorganic” component of 2D OIHs, while the “organic” component only improves the stability of 2D OIHs. We come up with an idea that functionalization on the “organic” component could open a door for designing new materials with much improved properties. We find that by introducing organic n-conjugate molecules, we can design a series of 2D OIHs with type II band alignment with two parallel high speed channels for hole and electron transfer, respectively. Remarkably, these 2D OIHs possess not only optimal bandgap, but also desirable optical absorption spectrum as well as high carrier mobility. Most importantly, we can modify the optoelectronic properties of these 2D OIHs by either changing halogen atoms, π-conjugate diaminoniums and/or layers of “inorganic” component for specific applications. These findings point out a new materials-design strategy for overcoming the charge-trap issue with the low-dimensional OIHs. We expect this work will draw broad attention from both organic and inorganic chemistry communities and materials science community.

SESSION ES17.06: New Physics in Halide Perovskites

8:30 AM *ES17.06.01
Exciton Spin Coherence in Hybrid Organic-Inorganic Perovskites Van Li; University of Utah, Salt Lake City, Utah, United States.

The hybrid organic-inorganic perovskites are an emerging class of semiconductors that have excellent optoelectronic properties, even being solution processed. These compounds also hold great promise for the field of spintronics due to their large and tunable spin-orbit coupling, spin-dependent optical selection rules, and predicted electrically tunable Rashba spin splittings. We demonstrate the optical orientation of spin-polarized excitons and spin coherence in polycrystalline films of MAPbI3 using time-resolved Faraday rotation measurement. The exciton spin coherence is manifested as oscillations of spin polarization in a transverse magnetic field, with a life time exceeding 1 ns at 4 K. The nanosecond spin coherence is quite surprising given that Pb and I exhibit large spin-orbit couplings. There are two frequencies in the oscillations show linear relationship with the transverse magnetic field, and the slopes give two g-factors which we assign to electrons and holes as g_e = 2.63, and g_h = 0.33. The energy dependence of the Faraday rotation follows the exciton absorption band at low temperatures, confirming its excitonic origin. However, exchange couplings of the excitons are very small (< 1 micro eV) in comparison to traditional semiconductors. We will discuss the possible spin relaxation mechanisms and unusual exciton spin physics.

9:00 AM *ES17.06.02
Spin-Orbital Coupling Effects in Perovskite Photovoltaic and Light-Emitting Devices Ranging from 3D to 2D Design Bin Hu; Materials Science and Engineer, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Organic-inorganic semiconductor perovskites have demonstrated very attractive room-temperature magneto-optical response, remarkable photovoltaic actions, high light-emitting properties, and low-threshold lasing actions, to become emerging multifunctional materials. On the other hand, organic-inorganic semiconductor perovskites possess a strong spin-orbital coupling within electrically polarizable semiconductor framework consisting of organic and inorganic components in ABX3 structure. In general, spin-orbital coupling can generate three major outcomes: (i) Rashba effect, (ii) spin mixing between different states, and (iii) electric-magnetic coupling in such hybrid perovskites. It should be pointed out that organic-inorganic semiconductor perovskites show significant orbital momentum to form a strong spin-orbital coupling with spin momentum. Therefore, using
orbital momentum presents a unique mechanism to tune the optoelectronic properties in such hybrid perovskites. We found that changing from 3D to 2D perovskites changes the internal interaction from short-range spin-spin interaction to long-distance orbital-orbital interaction, leading to distinct SOC effects on the populations on dark and bright states towards developing photovoltaic and light-emitting actions. On the other hand, we observed that the spin-orbital coupling can be changed by grain boundary polarization, leading to a convenient method to tune the spin-orbital coupling through doping and mechanical stress. Moreover, using the spin-orbital coupling presents a practical approach to remove the light-emitting loss from dark states in perovskite LEDs. In summary, this presentation will discuss the spin-orbital coupling effects involved in photovoltaic and light-emitting devices from 3D to 2D perovskites.

9:30 AM ES17.06.03 Computational Study of Polaron Emission in CsPbBr Nanocrystal Aaron Forde and Dmitri S. Klin; North Dakota State University, Fargo, North Dakota, United States.

Inorganic CsPbX₃ (X=Br,Cl) lead halide perovskites are of interest for photovoltaic and light-emitting applications due to long charge carrier diffusion lengths and tunability of the bandgap to generate photoluminescence (PL) with efficient quantum yields (QY). In the bulk morphology, the long charge carrier diffusion lengths are attributed to large polaron formation due to a ‘soft’ crystal lattice, which is inferred from infrared (IR) absorption. Polaron formation significantly reduces PL in films of CsPbX₃ NCs due to localization of photo-excited electrons and holes. A way to enhance IR polaron emission would be to confine the polaron which would significantly increase the spatial overlap of electron and hole states. CsPbX₃ nanocrystals (NCs) provide an excellent framework to explore the possibility of efficient IR polaron emission. Using a fully-passivated CsPbBr₃ NC atomic model, we compute spinor Kohn-Sham orbitals (SKSOs) with spin-orbit coupling (SOC) interaction as a basis to calculate efficiency of polaron emission. Efficiency of emission is determined from non-radiative recombination (kₚ) and radiative recombination (kᵣ) as kᵣ/(kᵣ + kₚ). Implications of this work provide framework for utilizing CsPbX₃ NCs as IR sensors.


9:45 AM ES17.06.04 Spin-Selectivie Light-Matter Interaction in Lead Halide Perovskites David Giovanni¹, Nirpan Mathews², ³, Subodh Mhasalkar², ³ and Tze Chien Sum¹; ¹School of Physical and Mathematical Sciences, Department of Physics and Applied Physics, Nanyang Technological University, Singapore, Singapore; ²School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore; ³Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore, Singapore.

Optical control of electron’s spin in a material system will lead to novel technological branch called as opto-spintronics. Conventional inorganic semiconductors (e.g. III-V and II-VI systems) face major challenges such as of lattice-matching and arduous fabrication processes. Moreover, optical spin control in most of these systems also requires cryogenic cooling. Herein, we propose lead halide perovskites as robust alternatives, where their band structures allows resonant excitation of 100% spin-polarized carriers/excitations. Few of their robustness to be highlighted: (i) ultra-large photoinduced Faraday rotation up to 10²°/μm in 3D perovskites, which is the largest reported up to our knowledge; and (ii) room-temperature tunable spin-selective optical Stark effect in 2D perovskites, which is a few times stronger than in the inorganic. Time-resolved studies on the spin-populations show that the spin-coherence live for a few ps in the 3D and few hundreds of fs in the 2D, due to Elliot-Yafet scattering and exciton exchange-interaction, respectively. Importantly, these works demonstrate robust optical control over spin-states, our result suggests the potential of perovskites for opto-spintronics applications.

10:00 AM BREAK

10:30 AM ES17.06.05 Epitaxy of Halide Perovskite Thin Films and Nanostructures Jian Shi; Rensselaer Polytechnic Institute, Troy, New York, United States.

Vapor-based epitaxial synthesis of halide perovskites remains rather limited. In this work, we present our recent progress in synthesizing epitaxial halide perovskite via a couple of epitaxy mechanisms. By van der Waals epitaxy, centimeter-scale in-plane interconnecting networks of CsPbBr₃ microwires and CsPb (Br₁, I₃₋ₓ) heterojunctions have been synthesized. By ionic epitaxy, single-crystalline CsPbBr₃ and CsSnI₃ films were grown on water-soluble NaCl substrates, which provides solutions for free-standing wafer-scale 3D-perovskite single-crystalline films. It is also shown that the concept of van der Waals epitaxy could be applied to the growth of Ruddlesden-Popper phase halide perovskite films. The epitaxial halide perovskites show unprecedented optoelectronic properties and phase transition behaviors.

11:00 AM ES17.06.06 Tuning Physical Properties of Halide Perovskites Using Composite Structures Hanwei Gao; Florida State University, Tallahassee, Florida, United States.

Halide Perovskites have shown potential for developing high-performance cost-effective optoelectronics. Previous work in this field was primarily focused on pristine perovskites. We discovered that perovskites in form of composites can exhibit more desirable physical properties with improved material stability. In this talk, I will discuss the correlation between material morphology and physical properties in composite halide perovskites, and their performance as light emitters.

11:30 AM ES17.06.07 Femtosecond Time-Resolved Excited State Dynamics at Interfaces and in the Bulk of MAPbI₃-xClₓ Clemens Burda; Chemistry, Case Western Reserve University, Cleveland, Ohio, United States.

The synthesis and excitonic properties of methylammonium lead halide perovskites and their mixed halides are presented with a focus on time-resolved photoluminescence and transient absorption spectroscopy. The substitution of a fraction of iodide with chloride anions leads to a distorted unit cell due to the smaller radius of the chloride anion relative to the iodide ion and thus to decreased symmetry and an increased band gap. Femtosecond laser induced transient absorption and photoluminescence measurements show that interface defects contribute to the relaxation processes in photoexcited perovskites. Under two-photon excitation, longer excited state lifetimes could be assigned to the lowest exciton with surprisingly different characteristics compared to the one-photon created states. Origins and implications of these materials properties will be discussed.

11:45 AM ES17.07.08 Tailoring Properties of Hybrid Perovskites by Domain-Width Engineering with Charged Walls Yurong Yang¹, ², Lan Chen³, Charles Paillard², Hong Jian Zhao¹, Jorge Iñiguez³ and Laurent Bellaiche³; ¹Nanjing University, Nanjing, China; ²University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States; ³Luxembourg Institute of Science and Technology, Alzette, Luxembourg.

Charged ferroelectric domain walls are fascinating electrical topological defects that can exhibit unusual properties. Here, in the search for novel phenomena, we perform and analyze first-principles calculations to investigate the electrical domain width on properties of domains with charged walls in the photovoltaic material consisting of methylammonium lead iodide hybrid perovskite. We report that such domains are stable and have rather low domain wall energy for any investigated width (that is, up to 13 lattice constants). Increasing the domain width first linearly decreases the electronic band gap from about 1.4 eV to about zero (which therefore provides an efficient band-gap engineering), before the system undergoes an insulator-to-metal transition and then remains metallic (with both the tail-to-tail and head-to-head domain walls being conductive) for the largest widths. All these results can be understood in terms of (i) components of polarization along the normal of the domain walls being small in magnitude; (ii) an internal electric field that is basically independent of the domain width; and (iii) rather negligibly charge transfer between walls. These findings deepen the knowledge of charged ferroelectric domain walls and can further broaden their potential for applications, particularly in the context of halide perovskites for photovoltaics.
The remarkable solar performance of lead halide perovskites can be attributed to their excellent physical properties that present many mysteries, challenges, as well as opportunities. Better control over the crystal growth of these fascinating materials and better understanding of their complex solid state chemistry would further enhance their applications. Here I will first report new insights on the crystal growth of perovskite materials and the solution growth of single crystal nanowires and nanoparticles of methylammonium (MA), formamidinium (FA), and all-inorganic cesium (Cs) lead halides perovskites (APbX₃) via a dissolution-recrystallization pathway. We also developed the epitaxial growth of perovskite materials and 2D heterostructures with controlled phases. Moreover, chemical strategies to stabilize the metastable perovskite phases, such as FAPbI₃ and CsPbI₂Br were developed by using surface ligands to manipulate the delicate thermodynamic and kinetic balance between 3D and 2D layered perovskites. We demonstrated high performance room temperature lasing with broadband tunability of emission with these single-crystal perovskite nanowires. The excellent properties of these single-crystal perovskite nanostructures of diverse families of perovskite materials with different cations, anions, and dimensionality make them ideal for fundamental physical studies of carrier transport and decay mechanisms, and for enabling high performance lasers, LEDs, and other optoelectronic applications.

Semiconductor quantum wells and superlattices, which are usually fabricated through metal-organic chemical vapor deposition or molecular beam epitaxy, are key building blocks in modern optoelectronics. The ability to simultaneously realize defect-free epitaxial growth and to individually fine-tune the chemical composition and band structure of each layer is essential for achieving the desired performance. Such structures are challenging to realize using organic or hybrid materials because of the difficulty of controlling the materials growth. In this talk, I will present a molecular approach to the synthesis of high-quality organic-inorganic hybrid perovskite quantum wells through incorporating widely tunable organic semiconductor building blocks. By introducing sterically tailored groups into the molecular motif, the strong self-aggregation of the conjugated organic molecules can be suppressed, and single crystalline organic-perovskite hybrid quantum wells (down to one mono-layer thick) and superlattices can be easily obtained via one-step solution-processing. Energy transfer and charge transfer between adjacent organic and inorganic layers are extremely fast and efficient, owing to the atomically-flat interface and ultra-small interlayer distance. The 2D hybrid perovskite superlattices are surprisingly stable, due to the protection of the bulky hydrophobic organic groups. The molecularly engineered 2D semiconductors are promising candidates for use in next-generation nanoelectronics, optoelectronics, and photonics.

Our study centered on perovskite core-shell structure and excitonic oscillator strength of perovskite nanocrystals. The optical response was studied to shed light on why the very poor light emitter CsPbBr₂ becomes a high-efficiency fast emitter when imbedded as nanocrystals in the wider gap host CsPbBr₃. Kinetics at a high carrier density of pure (extended) CsPbBr₂ and the nano-inclusion composite were measured and analyzed, indicating second order kinetics in extended and mainly first-order kinetics in the confined CsPbBr₂, respectively. Analysis of absorption strength of this perovskite imbedded nanocrystal composite relative to pure CsPbBr₂ indicated enhanced oscillator strength. We successfully implanted the CsPbBr₂-CsPbBr₃ core-shell structure into the application of light emitting diode. The type I heterojunction between CsPbBr₂ and CsPbBr₃ indicated multi-quantum wells structure which efficiently collected the carriers into the CsPbBr₂ nanocrystals for the high yield radiative recombination. We also demonstrated the CsPbBr₂ nanocrystals could be greatly stabilized by CsPbBr₃ solid matrix dramatically improving the device reliability. On the other hand, our study addressed the potential scintillator application of the perovskite core-shell single crystal.

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Crystal instability has been a major drawback hindering the commercialization of perovskite based devices. In this work, we demonstrate enhanced crystal stability and phase arrest at low temperatures in perovskite quantum dots, surface functionalized with 3-aminopropyl triethoxysilane. We studied temperature dependent crystal phase transitions in CH$_3$NH$_3$PbBr$_3$, Perovskite quantum dots (PQDs) ligated with octylamine bromide (P-OABr) and 3-aminopropyl triethoxysilane (P-APTES), using a framework of static and dynamic spectroscopy. P-OABr undergoes the expected structural phase transition from tetragonal to orthorhombic phase at ~140 K, established by the emergence of a higher energy band at 2.64 eV in the photoluminescence (PL) spectrum, while no phase transition was observed in the case of P-APTES. Such phase stabilization is a result of variation in their respective surface energies, an important contributing factor to the Gibbs free energy for nanomaterials. On further investigating the consequences of this altered crystal phase diagram using time-resolved PL, excitation power dependent PL and Raman microscopy over a range of 300 – 20 K, we observe significant differences in recombination rates and charge carrier types between P-APTES and P-OABr. Our findings highlight how aspects of PQD phase stabilization are linked to nanoscale morphology and the surface energy manipulation of the crystal phase diagram, providing critical insights into the synthesis of stable perovskite crystals for device implementation.

This work was supported by NASA MIRO grant No. NN15AQ01A.


4:15 PM ES17.07.06
Low Band Gap Lead Iodide Perovskite Nanocrystals and Their Application in LED Raihana Begum; Nanyang Technological University, Singapore, Singapore.

Perovskite nanocrystals of lead halide with an efficient absorption of UV-Visible and near-infrared light as well as their remarkable performance in optoelectronics devices have recently emerged as an extremely important class of semiconductor materials in both solar and optoelectronic communities. Despite the substantial developments in the synthesis and characterization of these nanocrystals, the low band gap nanocrystals, are not much explored perhaps due to their instability issues related to phase degradation. We have developed synthesis methods that yields high stability in terms of colloidal and phase stability for CsPbI$_3$ and FAPbI$_3$ nanocrystals, further we will also present our latest research on red LED and near infrared LED. In addition, we have recently demonstrated multiple exciton generation (MEG) from internally confined FAPbI$_3$ nanocrystals. So far, MEG from this material could not be achieved due to weak confinement. However, our nanocrystals (band gap <1.7 eV, emission >750 nm) are size-confined. The smallest of the FAPbI$_3$ NCs (7.5 nm) are found to be most efficient in MEG. The nanocrystals have small band gap with suitable confinement needed for MEG. For this, we have optimised the phase stabilization condition in order to achieve phase stability without any extrinsic doping. More importantly, by centrifugation at three different speed, we have been able to achieve homogeneous size distribution that overcome degradation by Ostwald ripening of NCs.

Reference

1. Low threshold and efficient multiple exciton generation in halide perovskite nanocrystals. Mingjie Li, Raihana Begum, Jianhui Fu, Qiang Xu, Teck Ming Koh, Sjoerd A. Veldhuis, Michael Grätzel, Niran Mathews, Subodh Mhaisalkar, Tze Chien Sum. Nature Communications 2018, 9, 4197; DOI: 10.1038/s41467-018-06596-1

4:30 PM ES17.07.07
Manipulating the Excited State of CsPbBr$_3$ Nanoplatelets for Superior Optical Properties Thomas Morgenstern; Matthew Jurow; Carissa N. Eisler; Jun Kang; Paul Alivisatos; Yi Liu; Wolfgang Brütting; Manual Engelward. 1University of Augsburg, Augsburg, Germany; 2Chemistry Department, University of California, Berkeley, California, United States; 3Molecular Foundary, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4MATERIALS Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Lead halide perovskite (LHP) nanocrystals (NCs) and their light emitting properties have recently moved into the focus of optoelectronic applications. Due to their narrow emission linewidths and high quantum yields, LHP NCs are promising materials for display and lighting technology. Especially within the blue emission regime, they could even outperform their organic counterparts. However many properties of emissive LHP nanoparticles remain to be investigated for a complete understanding of their optoelectronic properties.

One of the core concepts for efficient organic light-emitting diodes (OLEDs) is the preferential alignment of the emissive transition dipole moments within the emitting layer of the device. Using this effect the external quantum efficiency of purely organic devices can easily exceed 30%. However, within the context of LHP NCs this effect is rarely investigated. Recently the orientation of the emissive transition dipole of LHP nanocrystals could be determined to be vertical with respect to the film surface, hampering the maximum achievable quantum efficiency of LED applications.

To overcome this limitation we investigated the orientation of the emissive transition dipole moment of CsPbBr$_3$ nanoplatelets. Compared to their cubic counterpart, which do not show any form of quantum confinement, these NCs exhibit weak quantum confinement within the dimensions of the plates. This feature leads to huge differences in the optical properties of the excited state. As a first consequence the energy of the emission peak shifts to shorter wavelengths, resulting in an emission peak at 460nm for the investigated nanoplatelets. Further the orientation of the transition dipole moments is confined in space and therefore aligns within the plane of the substrate. Combined with the high refractive index of the perovskite material, the NCs have the potential to outperform existing solutions for blue emitting devices within display and lighting applications.


4:45 PM ES17.07.08
Continuous Flow Synthesis and Anion Exchange of Colloidal Perovskite Quantum Dots Milad Abolhasani; NC State University, Raleigh, North Carolina, United States.

Since the discovery of colloidal metal halide perovskite quantum dots (QDs) three years ago,[1] they have rapidly grown to become one of the most promising classes of nanomaterials for applications in low-cost and highly efficient optoelectronic devices. Anion exchange reactions of the highly luminescent perovskite QDs provide a facile post-synthetic route for tuning of the absorption/emission bandgap of these exciting nanocrystals. The post-synthetic anion exchange reactions allow precise bandgap tuning of perovskite QDs tailored for the desired application. Synthesis, screening, and optimization of colloidal QDs are conventionally conducted using the time- and material-intensive flask-based approaches. Process optimization is therefore limited by the sampling rate, off-line analysis time, and batch reactor/reaction process control. Batch reactors suffer from crystal instability has been a major drawback hindering the commercialization of Perovskite based devices. In this work, we demonstrate enhanced crystal stability and phase arrest at low temperatures in perovskite quantum dots, surface functionalized with 3-aminopropyl triethoxysilane. We studied temperature dependent crystal phase transitions in CH$_3$NH$_3$PbBr$_3$, Perovskite quantum dots (PQDs) ligated with octylamine bromide (P-OABr) and 3-aminopropyl triethoxysilane (P-APTES), using a framework of static and dynamic spectroscopy. P-OABr undergoes the expected structural phase transition from tetragonal to orthorhombic phase at ~140 K, established by the emergence of a higher energy band at 2.64 eV in the photoluminescence (PL) spectrum, while no phase transition was observed in the case of P-APTES. Such phase stabilization is a result of variation in their respective surface energies, an important contributing factor to the Gibbs free energy for nanomaterials. On further investigating the consequences of this altered crystal phase diagram using time-resolved PL, excitation power dependent PL and Raman microscopy over a range of 300 – 20 K, we observe significant differences in recombination rates and charge carrier types between P-APTES and P-OABr. Our findings highlight how aspects of PQD phase stabilization are linked to nanoscale morphology and the surface energy manipulation of the crystal phase diagram, providing critical insights into the synthesis of stable perovskite crystals for device implementation.

This work was supported by NASA MIRO grant No. NN15AQ01A.


2. Epps et al., Lab Chip 17, 4040–4047 (2017).
At the broadest level, the photoluminescence (PL) spectra of these materials show a massive Stokes shift compared to the corresponding absorption onset. Broadband emission is attributed to the formation of self-trapped excitons (STEs) due to the strong electron-phonon coupling. Interestingly, it has been observed in only certain three-dimensional and low-dimensional metal halide perovskites. In this talk, we will show how density-functional theory calculation that multiple STE structures exist in each perovskite exhibiting broadband emission. However, only the STE with Jahn-Teller like octahedral distortion is mainly responsible for the observed broadband emission, though it may not be the lowest energy structure. Our results provide important insights for designing perovskite materials for broadband emissions with preferred chromaticity coordinate or color temperature.

Prospects of widespread perovskite optoelectronics are contingent on the ability to exploit the unique photophysics of such class of materials for device functionality [1]. Photocarbonizing devices, like solar cells, as well as light-emitting ones, like LEDs and lasers, work best when non-radiative recombination is reduced, either by passivating traps and defects or by boosting radiative recombination rates. Concerning solar cells, the optimal Shockley-Queisser photoconversion efficiency is achieved precisely in the radiative limit, when the only carrier loss is optical emission. We demonstrate a technique, based on the absolute photoluminescence quantum yield as a function of the excitation intensity, to measure the photoconversion open circuit voltage (the free energy) and the ideality factor without any current flowing through the film [2]. A picture emerges of selective traps creating unbalanced free electron and hole populations, universally shared by perovskite materials with various compositions and fabrication routes. We identify interfaces or materials that are the limiting the solar cell photocathedral efficiencies and highlight a rational method to optimize solar cells.

The very nature of the optical emission process in perovskites, whether it comes from a direct or indirect bandgap, is actively debated, as recent studies have proposed that the Rashba spin orbit coupling gives rise to an indirect gap, few tenths of meV lower in energy than the direct one. The instantaneous intensity of photoluminescence under pulsed excitation provides measurements for the radiative recombination rates in halide perovskites and shows that radiative recombination becomes faster with decreasing temperature, as in all direct bandgap materials and contrary to what expected for 3D Rashba semiconductors [3]. As for strategies to boost light emission at low excitation levels, carrier confinement enhances local concentration of photoexcitations either in mixed 2D-3D materials or quantum-dot-in-a-matrix architectures, where a low concentration of localized excited states can be filled efficiently even by photoexcitation even in the low excitation regime [4], leading to efficient LEDs or low-threshold lasers.

Given the major progress achieved in perovskite devices by understanding their photophysics, deployment of optical spectroscopy tools will provide crucial guidance for the understanding of the ultrafast dynamics and sub-picosecond processes observed in photoexcited perovskites.

References

Element-Specific Contributions to the Electronic Structures of Inorganic Cesium Lead Halide Perovskites Revealed by Resonant X-Ray Photoelectron Spectroscopy
Xuechen Jiao, 1, 2, 3, 4
1 University of Melbourne, Melbourne, Victoria, Australia; 2 Australian Synchrotron, Australian National University and Technology Organisation, Melbourne, Victoria, Australia.

Inorganic cesium lead halide perovskites (such as CsPbBr$_3$) constitute an emerging class of high performance semiconducting materials, delivering promising device performances in solar cells and light emitting devices. Despite the rapid development of device optimisation, many fundamental issues remain open. One of the questions attracting huge attention is: do the constituent elements contribute equally to the electronic structures of perovskites? To address this, synchrotron-based resonant photoelectron spectroscopy (resPES) was employed to resolve the low binding energy region from -5 eV to 100 eV (valence band and shallow core levels) of a model inorganic perovskite material – CsPbBr$_3$, which delivers high air stability and satisfactory solar cell performance. Taking advantage of the energy tunability provided by synchrotron, the incident X-ray energy was tuned around the absorption edges of the component elements, including Cs, Pb, Br, and I. With the high-resolution photoelectron spectroscopy at the low binding energy
region from -5 eV to 100 eV, it was found that the photomission cross-sections at the shallow core levels of the constituent elements and valence band region follow different trends when the incident X-ray energy was tuned toward the absorption edges of different elements. Intriguingly, additional photoemission bands emerged around the valence band region when Cs²⁺ was selectively excited, while the X-ray excitations around other constituent elements do not show such extra photoelectron bands. With the aid of resPES, direct experimental evidence was obtained to support that different constituent elements contribute, in a dissimilar way, to the electronic structure of inorganic cesium lead halide perovskites. This exciting work is believed to be able to experimentally verify or disapprove the proposed electronic structure models of high performance perovskite materials.

10:15 AM BREAK

10:45 AM *ES17.08.06
Photophysical Properties of Perovskite Thin Films, Microcrystals and Nanocrystals Hernán Míguez, Andrea Rubino, Mauricio Calvo, David Tiede and Juan Galisteo; Consejo Superior de Investigaciones Científicas, Instituto de Ciencia de Materiales de Sevilla, Seville, Spain.

A description of the photophysical properties of perovskite thin films, microcrystals and nanocrystals, and their dependence with the chemical and optical environment, will be provided. The exposure of thin films and microcrystals to different atmospheres has a strong effect on their photoemission, which reveals relevant information about the mechanism behind ion migration, one of the most intriguing observations reported for these semiconductors [1,2,3] A detailed analysis of the processes triggered by photoexcitation that lead to activation and latter deactivation of luminescence will be presented. Also, it will be shown that precise control of the spectral features of the luminescence, along with enhanced stability, can be achieved from perovskite microcrystals synthesized in different types of nanoporous matrices [4,5] Interestingly, under these conditions, increase of the photoluminescence quantum yield results from the improved optical environment they are exposed to [6] All this opens the door to the development of novel color converting coatings of application in LED technology, as it will be demonstrated in this talk.

References

11:15 AM ES17.08.07
Transport Properties of All-Inorganic Perovskite CsPbX₃ Nanocubes—Developed by a Facile Room Temperature Surfactant-Mediated Emulsion Approach Sayantani Das; Department of Physics, Jadavpur University, Kolkata, India.

Inorganic-organometallic halides with perovskite structures (ABX₃) have emerged as novel materials because of their unique properties of high absorption coefficients, balanced electron/hole mobility, possible low temperature processing, small exciton binding energies and long exciton diffusion lengths [1, 2]. Here we have developed uniform sized, nano-cube shaped, inorganic perovskite nanocrystals via a facile room temperature surfactant-mediated emulsion approach which may lead to opportunity for different applications like lasing, light-emitting diodes, solar cells, photo detectors etc. The samples we have prepared are all inorganic perovskite nanocubes of CsPbX₃ where the cation A is Cs⁺, B is a bivalent metal cation Pb²⁺ and X is a halide, usually CI⁻; Br⁻ and/or I⁻. Surface morphology and crystallinity of the synthesized samples are examined by field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) analysis gives the confirmation of the phase structure of the samples. To attain further crystallinity confirmation we have carried out high resolution transmission electron microscope (TEM) analysis. UV-visible spectra are recorded in reflectance mode and band gap (Eg) is estimated for the samples. The optical properties (band gap and photoluminescence behaviour) of CsPbX₃ are enhanced significantly in nano cube sample as compared to the bulk CsPbX₃ samples. Elemental composition of the sample is investigated via EDX analysis. These single crystalline nanocubes crystallize in orthorhombic phase and exhibit strong photoluminescence emission too.

References

11:30 AM *ES17.08.08
Impact of Monovalent Cation in Metal Halide Perovskites on Monomolecular and Bimolecular Charge Recombination Benjamin Foley¹, Katelyn Dagnall¹, Ying-Zhong Ma² and Joshua Choi³; ¹University of Virginia, Charlottesville, Virginia, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Monomolecular and bimolecular recombination constants in metal halide perovskite thin films of various monovalent cations with consistent morphology and charge trap density were studied. Our results reveal that the monovalent cation plays different roles in monomolecular and bimolecular recombination, indicating that the remarkably customizable metal halide perovskites may be more tunable than previously thought.

SESSION ES17.09: Compositions and Structures of Halide Perovskites
Session Chairs: Steve Cranford and Michael Saliba
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 131 B

1:30 PM *ES17.09.01
The Versatility of Polyelemental Perovskite Compositions Michael Saliba; Adolphe Merkle Institute, Fribourg, Switzerland.

Perovskites have emerged as low-cost, high efficiency photovoltaics with certified efficiencies of 22.1% approaching already established technologies. The perovskites used for solar cells have an ABX₃ structure where the cation A is methylammonium (MA), formamidinium (FA), or cesium (Cs); the metal B is Pb or Sn; and the halide X is Cl, Br or I. Unfortunately, single-cation perovskites often suffer from phase, temperature or humidity instabilities. This is particularly noteworthy for CsPbX₃ and FAPbX₃, which are stable at room temperature as a photoinactive “yellow phase” instead of the more desired photovoltaic “black phase” that is only stable at higher temperatures. Moreover, apart from phase stability, operating perovskite solar cells (PSCs) at elevated temperatures (of 85 °C) is required for passing industrial norms. Recently, double-cation perovskites (using MA, FA or Cs, FA) were shown to have a stable “black phase” at room temperature. These perovskites also exhibit unexpected, novel properties. For example, Cs/FA mixtures suppress halide segregation enabling band gaps for perovskite/silicon or perovskite/perovskite tandems. In general, adding more components increases entropy that can stabilize unstable materials (such as the “yellow phase” of FAPbI₃) that can be avoided using the also unstable CsPbI₃. Here, we take the mixing approach further to investigate triple cation (with Cs, MA, FA) perovskites resulting in significantly improved reproducibility and stability.
engineering as a strategy to integrate the seemingly too small rubidium (Rb) (that never shows a black phase as a single-cation perovskite) to study novel multication perovskites. (5)

One composition containing Rb, Cs, MA and FA resulted in a stabilized efficiency of 21.6% and an electroluminescence of 3.8%. The Voc of 1.24 V at a band gap of 1.63 eV leads to a very small loss-in-potential of 0.39 V, one of the lowest measured on any PV material indicating the almost recombination-free nature of the novel compound. Polymer-coated cells maintained 95% of their initial performance at 85°C for 500 hours under full illumination and maximum power point tracking. This is a crucial step towards industrialisation of perovskite solar cells.

Lastly, to explore the theme of multicomponent perovskites further, molecular cations were revaluated using a globularity factor. With this, we calculated that ethylammonium (EA) has been missclassified as too large. Using the multication strategy, we studied an EA-containing compound that yielded an open-circuit voltage of 1.59 V, one of the highest to date. Moreover, using EA, we demonstrate a continuous fine-tuning for perovskites in the “green gap” which is highly relevant for lasers and display technology. The last part elaborates on a roadmap on how to extend the multication to multicomponent engineering providing a series of new compounds that are highly relevant candidates for the coming years. (6)

(3) McMeekin et al. Science (2016)
(4) Saliba et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. Energy & Environmental Science (2016)
(6) Turren-Cruz et al. Methylammonium-free, high-performance and stable perovskite solar cells on a planar architecture Science (2018)

2:00 PM ES17.09.02
Atomic Scale Analysis of Perovskite MAPbI\textsubscript{3} for Light Emitting Applications
Afshan Jamshaid, Robin Ohmann, Jeremy Hieulle, Collin Stecker, Luis K. Ono and Yabing Qi; EMSSU, Okinawa Institute of Science & Technology, Onna, Japan.

In recent years, the organic-inorganic hybrid perovskite has gained an increasing research interest in academia for applications in highly efficient thin film solar cells and LEDs, due to the low-cost fabrication process, low non-radiative recombination, tunable bandgap \( [\text{1}] \), and material availability \( [\text{2}] \). For highly efficient LEDs, the highly uniform ultra-flat films with nanometer-sized grains are required. Among the hybrid perovskites, MAPbI\textsubscript{3} (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}) based LEDs has shown high efficiency but with several obstacles such as instability of un-encapsulated LEDs, and hysteresis loss. Therefore, commercialization of these LEDs is still a challenge. Understanding and resolving these issues necessitates the investigation of the perovskite thin films at the atomic scale to determine the underlying fundamental processes. Here, we present the growth and experimental characterization of thin MAPbI\textsubscript{3} films on Au \((111)\) under ultra-high vacuum conditions. The thin films were prepared by vacuum evaporation of the precursor molecules MAI and PbI\textsubscript{2}, with a thickness of a few monolayers (approx. 4 nm). We characterize the sample with scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS), obtaining information about the atomic structure, and chemical composition. For the electronic properties analysis, we used Ultraviolet photoemission spectroscopy (UPS), and Inverse Photoemission spectroscopy (IPES). Our study will provide the basis for further exploration of mixed perovskite materials for the future highly efficient LED applications.

References

2:15 PM ES17.09.03
Lead-Halide Perovskite Surface Defects and Their Implications for Device Interface Engineering
Collin Stecker\textsuperscript{1}, Kexi Liu\textsuperscript{1}, Jeremy Hieulle\textsuperscript{1}, Zhengyu Liu\textsuperscript{2}, Robin Ohmann\textsuperscript{1}, Luis K. Ono\textsuperscript{1}, Guofeng Wang\textsuperscript{3} and Yabing Qi\textsuperscript{1}; Okinawa Institute of Science and Technology, Okinawa, Japan; \textsuperscript{2}Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Lead-halide perovskites are an exciting new class of low-cost semiconductors with optoelectronic properties suitable for LED applications. MAPbI\textsubscript{3} has been utilized to create LEDs with an external quantum efficiency of 9.3\% (Xiao et al., 2017) However, defects in perovskite films can affect device performance. It has been hypothesized that vacancy defects are MABr vacancies and that vacancy defects at the surface of the film change the local work function, which has important implications for energy level alignment between layers in an LED device.

References

2:30 PM ES17.09.04
Pressure-Induced Dramatic Changes in Structures and Optoelectronic Properties of Halide Perovskites
XuJie Li; Center for High Pressure Science and Technology Advanced Research, Beijing, China.

Metal halide perovskites have emerged as a promising family of functional materials for advanced optoelectronic applications with high performance and low costs. Various chemical methods and processing approaches have been employed to modify the compositions, structures, morphologies, and electronic properties of hybrid perovskites, great progress has been achieved. Whereas, challenges still remain such as the low stability, the use of environmentally unfriendly chemicals, and the lack of an insightful understanding of the structure-property relationships. In this talk, we will present our efforts in using an alternative means, pressure, to tune the structures and physical properties of halide perovskites. Using state-of-the-art high-pressure techniques coupled with \textit{in situ} synchrotron-based and in-laboratory property measurements, we characterized the changes in their structural, electrical, and optical properties. Pressure-sensitive enhanced properties such as higher electron transport and stronger light absorption, as well as pressure-induced novel phenomena, were observed. Our findings reveal that high pressure can potentially be able to realize enhanced and/or emergent properties of halide perovskites, and further our understanding of the structure-property relationships.

2:45 PM ES17.09.05
Atomic Structure and Electrical Activity of Planar Faults in Cesium Lead Bromide Perovskite
AraSheeep S. Thind\textsuperscript{1}, Guangfu Luo\textsuperscript{2}, Jordan A. Hachtel\textsuperscript{2}, Maria V. Morrell\textsuperscript{2}, Sung B. Cho\textsuperscript{2}, Albina Y. Borisevich\textsuperscript{1}, Juan C. Idrobo\textsuperscript{3} and Rohan Mishra\textsuperscript{2, 1}; \textsuperscript{1}Institute of Materials Science & Engineering, Washington University in St. Louis, St. Louis, Missouri, United States; \textsuperscript{2}Department of Mechanical Engineering & Materials Science, Washington University in St. Louis, St. Louis, Missouri, United States; \textsuperscript{3}Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; \textsuperscript{4}Department of Chemical Engineering, University of Missouri, Columbia, Missouri, United States.

Lead-halide perovskites have emerged as a promising class of highly efficient and affordable semiconductors with applications in solar cells and optoelectronic devices. One of the...
key features of these lead-halide perovskites is their ability to retain their performance even in the presence of a large concentration of defects that are generated from their fast solution-based synthesis. Point defects in lead-halide perovskites either lead to shallow defects levels or resonant levels within the valence or conduction bands, which allow efficient carrier transport. In addition to point defects, the solution-deposited polycrystalline perovskites also have a large concentration of planar defects, such as grain boundaries. These defects are critical to the charge transport and electron-hole recombination characteristics of a semiconductor, and therefore, to the overall device performance. Nevertheless, there are diverging reports on the electrical activity of grain boundaries in lead-halide perovskites. While some reports have suggested them to be benign or even beneficial for charge separation and transport, others have suggested them to be detrimental. A major reason of this controversy lies in the fact that, till date, there have been no experimental reports on the atomic structure and composition of planar defects in these materials.

We have combined aberration-corrected scanning transmission electron microscopy (STEM) and first-principles density-functional theory (DFT) calculations to image grain boundaries and other planar faults in CsPbBr3 nanocrystals and elucidate their impact on the electronic properties. We have employed a novel post-synthesis process to trigger the formation of as-synthesized nanocrystals that leads to the formation of planar faults. Using atomic resolution STEM we observe that the fusion process is accompanied by the formation of predominantly two types of planar faults: previously unreported Br-rich $\Sigma_3$ grain boundaries and Ruddlesden-Popper (RP) planar faults. Generally, in conventional semiconductors planar defects — such as grain boundaries — can be detrimental to their performance as they can introduce mid-gap states, which act as nonradiative recombination centers. However, using DFT calculations we find that neither of the planar faults observed in CsPbBr3 induce deep defect levels, but their Br-deficient counterparts do. We find that the $\Sigma_3$ grain boundaries repel electrons and attract holes, similar to an n-p-n junction, while the RP planar defects repel both electrons and holes, similar to a semiconductor-insulator-semiconductor junction. We will discuss the implications of these findings along with strategies to improve the performance of lead-halide perovskites by tailoring the planar faults, in fact, to achieve stable photoluminescence.

Acknowledgments: This work was supported by NSF grant DMR-1806147. This work used computational resources of the Extreme Science and Engineering Discovery Environment, which is supported by the NSF grant number ACI-1053575. A portion of the STEM experiments was conducted at the Center for Nanophase Materials Sciences at Oak Ridge National Laboratory (ORNL), which is a Department of Energy (DOE) Office of Science User Facility, through a user project (J.A.H. and J.C.I.).


3:00 PM BREAK

3:30 PM +ES17.09.06 Photophysical Properties of Materials Composition Tunable and Doped Colloidal Perovskite Nanocrystals Joseph Luther1, Abhibit Hazarika1, Ashley Gaulding1, Qian Zhao1, 2, Mokshin Suri3, 2 and Taylor Moot1; 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2College of Chemistry, Nankai University, Tianjin, China; 3University of Texas, Austin, Austin, Texas, United States.

Colloidal Perovskite Quantum Dots (QDs) have some outstanding optoelectronic properties. Here we present results on such properties of perovskite QDs in solution and in films measured through a variety of optical and electrical techniques. Such Perovskite QD solar cells show high $V_{OC}$ of 90% of their maximum in the radiative limit, but also show promise in non-PV applications such as light emitters for LED, lasing, displays, or sensing such as photoFETs, which will be the focus of this talk. Perovskite QDs possess unique properties that are not accessible in their bulk or thin-film counterparts. For example, inorganic perovskite materials of CsPbI3 are unstable in ambient condition in bulk or thin-films, but they are phase stable in their quantum confined form. Another interesting advantage of these QD materials is that their compositions can be tuned without changing the crystal framework either by direct synthesis or by post-synthetic ion exchanges. Particularly, X-site ion exchange in the perovskite QDs with general formula ABX3 (where A= Cs, Cs–methanimmonium–MA, formamidinium–FA etc., B= Pb or Sn; X= Cl, Br, I) has shown to be very facile. On the other hand, A-site composition tunability is very limited in these materials, or even in very thin films. For example, high FA concentration Cs8,FA,Pb3 has not previously been demonstrated in either QDs and thin films, and it has been shown that only compositions with (1-x)<0.4 can be realized in the pure usable perovskite phase. This is due to thermal instability of FAPbI3 at temperatures required to crystallize CsPbI3 (above 300 °C). However, we present a simple post synthetic cross-cation exchange reaction between colloidal solutions of CsPbI3 and FA-Pb nanocrystals just by mixing them at temperatures slightly above the room temperature that enables us to achieve compositions in the whole range of 0<x<1. This helps us to realize compositions that were not known previously. The photoluminescence (PL) kinetics studies reveal that the activation energy required to inter-exchange the Cs+ and FA+ ions is around 0.65 eV, higher than that for X-site exchange in lead halide perovskites. We have studied a wide range of perovskite QD compositions with time resolved photoluminescence and microwave conductivity as well as studied the application toward photosensing FETs.

4:00 PM ES17.09.07 On the Chemical Origins of Crystalline Orientations in Hybrid Perovskite Thin Films—Microstructures Revisited Shambhu Pratap1, 2, Johannes Schlipf1, Lorenz Bielmann1 and Peter Müller-Buschbaum1; 1Technische Universität München, München, Germany; 2Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Technische Universität München, Heinz-Maier-Leibniz Zentrum (MLZ), München, Germany.

Mixed perovskites towards high efficiency photovoltaics have been pioneered in the photovoltaic community and extensive efforts have been made in order to enable the technology. The impact however, of chemical mixing of such dynamic systems on the morphological structures is largely understudied. Within our study we show that not only does chemical engineering of perovskites affect electronic structure within the material, but the colloidal precursor of the material behaves in strongly dynamic ways and leads to the emergence of intense hierarchical structures within thin films. The phenomenon is similar to those within vivid natural and material systems. Unlike other studies which emphasize on refining film morphologies, we explain the science behind the emergence of natural microstructures, with the aim of elucidating the inherent behaviour of perovskite precursors, which would assist in better understanding and treatment of the material and its properties. We utilize simple and highly intuitive measurements (microscopy and scattering) which strongly support the natural and can be easily understood by a broad range of scientists and engineers- spanning from those interested in photovoltaic material processing, colloidal and soft materials, fluid dynamics, pattern formation, crystallography, to name a few. We explain the emergence of different length scales of film microstructure from different perspectives and how they all are intertwined and dependant on the lowest common multiple of all systems- thermodynamics and energetics, during non-equilibrium conditions.

4:15 PM ES17.09.08 Revealing Cations Locations and Their Impact on the Properties of Mixed MAxCs1−xPbBr3 Perovskite for Light Emitting Diode Application Jeremy G. Hieule1, Shulin Luo2, Afshan Jamshaid2, Collin Stecker1, Robin Ohmann1, Luis K. Ono3, Lijun Zhang4 and Yabing Qi4; 1Okinawa Institute of Science and Technology Graduate University (OIST), Onna, Japan; 2Key Laboratory of Automobile Materials of MOE and College of Materials Science and Engineering, Jilin University, Changchun, China.

Metal halide perovskites are an emerging class of semiconductor with a great potential for use in optoelectronic devices. Recent work, reported the formation of a perovskite based light-emitting diode with external quantum efficiency (EQE) exceeding 20% [1]. This record EQE for perovskite based technology was achieved by managing the compositional distribution in a CsPbBr3/MABr system, to provide high luminance and balanced charge injection. The MABr species is suggested to passivate defects and grain boundaries in the perovskite film. However, the exact location of the methylammonium species and its interplay with the perovskite lattice is still unclear. Therefore, the determination of the diffusion and the control of the perovskite morphology [2] as well as the locations of the cations in the material are of prime importance for developing perovskite-based LED with high EQE.

In this work, combining scanning tunneling microscopy (STM) and density functional theory (DFT), we reveal the exact location of MA (CH3NH3) and Cs cations in MAx,Cs1−xPbBr3 mixed perovskite lattice at the atomic scale. Additionally, using UV/X-ray photoelectron spectroscopy (UPS/XPS), we demonstrate the impact of cations mixing on the material electronic properties. The understanding of the structure/property relationship in mixed MAx,Cs1−xPbBr3 cations perovskite provide new tools for the precise design of light emitting devices.
HALIDE PEROVSKITES (HPs) are a large family of fascinating semiconductor materials that have revolutionized the field of optoelectronics. While the bandgap of HPs is highly tunable, the HPs that are mostly studied have bandgaps over 1.4 eV in general. It is highly demanded to develop HPs with bandgaps below 1.4 eV for certain optoelectronic applications such as infrared-light-emitting devices and photodetectors. Here, we have provided rational materials-design approaches for achieving halide perovskites that not only exhibit low-bandgaps (<1.4 eV), but also have high stability for potential device applications. The formation mechanisms of these materials are discussed in details.

References:

SESSION ES17.10: Nanocrystals and Single-Crystals of Halide Perovskites

Session Chair: Zhijun Ning
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 131 B
An intriguing reversible band gap narrowing behavior of the lead-free hybrid perovskite single crystal DMASnI (DMA = CH3NHCH3) from yellow to black is observed without oxidation and phase transformation. We discuss the transformation mechanism in detail. More interestingly, the transformed samples in black can rapidly self-heal into yellow ones when exposed to deionized water (DI water). Contrary to other hybrid perovskites, DMASnI crystals exhibit excellent water phase stability. For example, DMASnI was immersed in DI water for 16 h and no decomposition was observed. Inspired by its excellent water phase stability, we demonstrate a potential eco-friendly application of DMASnI in photo-catalysis for H2 evolution in DI water. We present the first H2 evolution rate of 0.64 μmol h−1 with good recycling properties for pure DMASnI crystals. After the narrowing process, the optical band gap of DMASnI can be lowered from 2.48 eV to 1.32 eV. Systematical characterizations are applied to investigate their structural and optoelectronic properties. The reversible band gap narrowing behavior and outstanding electrical properties, such as higher carrier mobility and longer carrier lifetime show that DMASnI has a great potential for optoelectronic applications.

10:00 AM BREAK

10:30 AM ES17.10.05

Inorganic Halide Perovskite Single Crystal—Growth Mechanism, Structural and Optical Properties Sovesh Mohapatra, Naveen K. Tailor and Soumitra Satapathi; Indian Institute of Technology, Roorkee, India.

Lead halide semiconductors with a perovskite crystal structure and APbX3 stoichiometry (A = Cs+, Rb+, or K+, X = Cl, Br, or I) are well known for their potential use in optoelectronic devices. In this work, we demonstrate the growth of inorganic lead halide perovskite single crystals (NCs) via a conventional ion-exchange method using parent compounds of CsPbX3. The single crystal XRD, UV-Vis, PL, and TSPC results show the high quality of the synthesized single crystals. The band gap energies of these nanocrystals were tuned from 2.02 eV to 3.00 eV, which is the highest band gap of lead halide perovskite single crystals. The PLQYs of these nanocrystals were over 90%, which is the highest value for lead halide perovskite single crystals. The tunability of the band gap and the high PLQYs make these single crystals potential candidates for optoelectronic applications.

Lead-based inorganic metal halide perovskite materials have the general chemical formula of CsPbX3, where X is Cl, Br, or I. The electronic and optical properties of metal halide perovskites (MHP), such as narrow emission wavelengths, readily adjustable emission wavelengths, and high photoluminescence quantum yields (PLQYs) are advantageous for a number of different optoelectronic devices, including photovoltaics, lasers, and light emitting diodes. Though synthesis and anion-exchange of MHPs are relatively facile, synthesized MHP nanocrystals (NCs) via typical ion-exchange methods show instability in air and moisture, and PLQYs of MHPNCs decrease over time due to a continuous loss of labile parent surface ligands. To enable the further development and application of MHPNCs, the stability must be increased while maintaining or improving high PLQYs. Herein, we report a fast and simple anion-exchange reaction for MHPNCs using allylchlororosilane (RSLCl) at room temperature (20°C-22°C), with motivation stemming from the ability of the allylchlororosilane to both provide the chloride for the anion exchange while also forming a protective stabilizing siloxane shells around the exchanged NCs. In this study, we show that colloidal host CsPbBr3 NCs transform into colloidal CsPbCl3 NCs upon exposure to RSLCl due to the anion-exchange reaction between Br of CsPbBr3 and Cl of RSLCl. Both colloidal and solid thin films of CsPbCl3 NCs produced with allylchlororosilane show good moisture stability and relatively high PLQYs of ~13%, whereas colloidal CsPbBr3 NCs produced via typical methods show low PLQYs (1-10%) and degrade rapidly upon exposure to moisture or ambient air.

11:00 AM ES17.10.07

Properties of 2D/3D Halide Perovskites with Organic Conjugated Cations Ivan Mora-Serio; Universität Jaume I, Castelló de la Plana, Spain.

Two-dimensional (2D) hybrid perovskites (HPVKs) are structures alternating organic and inorganic layers, arising from inclusion of a large organic cation providing Goldschmidt’s tolerance factor higher than 1. This fact generates separation of a determined number of inorganic layers (n), which can range from 1 to ∞, which corresponds to a 3D arrangement. A variation of this pure organic—inorganic structure can be obtained by addition of a small organic cation, MA (CH3NH3+) in most cases, providing a cavity is supported by single-crystal XRD and structural determination of select compounds. The facile ligand assisted reprecipitation method to synthesize colloidal nanoplatelets of Ruddlesden-Popper lead halide perovskites is characterized by high PLQYs and stability. In this study, we demonstrate the successful tunability of dielectric confinement by the inclusion of a conjugated molecule, anilinium cation, as a bulky cation, in the fabrication of the 2D/3D PVK material (C6H5NH3)2(CH3NH3)n-1PbnI3n+1, where n=3-5.

11:15 AM ES17.10.08

Colloidal Nanoplatelets of Ruddlesden-Popper Lead Halide Perovskites Containing Various A-site Cations Matthew P. Hautzinger; Alexis Peggs; Dongceu Pan; John Wright; and Song Jin; Chemistry, University of Wisconsin—Madison, Madison, Wisconsin, United States; 2Dillard University, New Orleans, Louisiana, United States.

The structure of organic-inorganic lead halide perovskites (APbI3) has been limited by geometric considerations to what cation can occupy the A-site cavity. Here we have continued to expand beyond this A-site limit by synthesizing colloidal nanoplatelets of the structurally labile Ruddlesden-Popper perovskites (\(A\:A\'_n \text{Pb}_n \text{I}_{3n+1}\)) containing a series of new large A-site cations, such as ethylammonium (EA), as well as the commonly observed methylammonium (MA), formamidinium (FA) and cesium. The flexible lattice of the Ruddlesden-Popper’s structure allows the introduction of large A-site cations into the perovskite A-site cavity. The occupancy of these large A-cations in the perovskite A-site cavity is supported by single-crystal XRD and structural determination of select compounds. The facile ligand assisted reprecipitation method to synthesize colloidal nanoplatelets of (EA)n(A)PbI3 with varying A-cations was utilized as a convenient pathway to explore more exotic cations. The nanoplatelets are 100-200 nm in lateral dimension and exhibit clear quantum confinement structure. Optic characterization demonstrates strong photoluminescence as well as a strong excitonic feature in the absorbance spectra. The A-site cation is shown to have an impact on the absorbance onset position, PL peak position, QY, and lifetimes. This work highlights a pathway to synthesizing model systems as a way to systematically compare the impact of the A-site cations role in the optoelectronic properties of lead halide perovskites.
Solution-processable perovskites have recently emerged as extraordinary semiconductor materials for light-emitting diodes (LEDs). So far most of the high efficiency LEDs have been demonstrated on small area and by employing difficult-to-control anti-solvent engineering techniques, whereby the required processes do not permit uniform coating over a large area, hindering the potential commercialization of the technology in large area lightings and display devices. Here we report a scalable method to deposit large-area and uniform nanostructured perovskite thin film for active layer in LEDs. The large area deposition is enabled by the pre-synthesized colloidal nanocrystal inks, which allows the formation of unique self-assembled perovskite nanostructure featuring 3D formamidinium lead bromide (FAPbBr3) nanocrystals of graded size coupled with microplatelets of octylammonium lead bromide perovskites. The nanostructure thin film, formed by a simple spincoating deposition of colloidal inks, exhibits photoluminescence quantum yields of over 80%, enabled by the energy cascading effect that significantly improve bimolecular recombination properties at lower charge injection density. Our small area (3 mm2) LEDs reach high external quantum efficiency exceeding 13% and brightness above 50k cd m−2. Moreover we also demonstrate large area LED (≤5 cm2) with a uniform emission and high brightness (>20k cd m−2). These results demonstrate the benefits of the pre-synthesized colloidal inks for fabrication of large area LEDs.

11:45 AM ES17.10.10
Chemical Vapor Transport Deposition of Stable Cubic CsPbI3 Optical Films on Porous Alumina Substrate Cong Zhao1, Shichao Zhao2, Yuanfang Zhao1, Fang He1, Jingzhou Li1, Shixi Zhao1, Feiyi Kang1, and Guodan Wu1; 1Tsinghua-Berkeley Shenzhen Institute, Tsinghua University, Shenzhen, China; 2College of Materials & Environmental Engineering, Hangzhou Dianzi University, Shenzhen, China; 3Graduate School at Shenzhen, Tsinghua University, Shenzhen, China.

Cesium lead iodide perovskite (CsPbI3) with excellent optical and electrical properties have attracted numerous academic attentions. Specifically, the black cubic phase CsPbI3 with a direct band gap of 1.74 eV has been most appropriate materials for various optoelectronic applications, especially for photovoltaic (PV), Light-Emitting Diodes (LED) and photodetector applications. However, the preferred cubic phase of bulk CsPbI3 (α-CsPbI3) is usually only stable at high temperatures and it will undergo an immediate phase transformation to orthorhombic phase (δ-CsPbI3) after fabrication at room temperature. Attempts to stabilize the cubic phase in ambient temperature have been focused on complicated procedures such as quantum dot-induced films, poly-vinylpyrrolidone (PVP)-induced surface passivation engineering and chemical composition tuning. In the meantime, most of current efforts have been focused on solution process. Up to now, it has been still a challenge to synthesize the CsPbI3 through chemical vapor deposition (CVD) method. In this work, we have discovered a convenient CVD method to investigate the growth behavior of the cubic α-CsPbI3 film on the porous alumina substrate. The lead iodide and cesium iodide were used as the precursors for the deposition of CsPbI3. The effect of CsPbI3 with high surface area and large pore volume was used as growth substrate. It was shown that the porous alumina promoted the growth of CsPbI3 film by absorbing the precursor and increasing the nucleation density. The prepared CsPbI3 film emitted strong and stable red light (ca. 1.9 eV) under ultraviolet light excitation and room temperature ambient atmosphere. The lead iodide was absorbed on the surface of the porous alumina firstly then reacted with cesium iodide to form the CsPbI3. The successful preparation of the CsPbI3 by the CVD method paves the way for its large scale growth and application in optoelectronic devices.

SESSION ES17.11: Frontier Phenomena of Halide Perovskites
Session Chairs: Ivan Mora-Sero and Yuanyuan Zhou
Friday Afternoon, April 26, 2019
PNC Corridor, 100 Level, Room 131 B

1:30 PM ES17.11.01
PN Junction of a Thin-Film Perovskite Daniel Ramirez and Dmitri S. Kilin; Chemistry & Biochemistry, North Dakota State University, Fargo, North Dakota, United States.

Lead-halide perovskites exhibit favorable properties when compared to conventional optoelectronic materials. The single-crystalline hybrid perovskites have important photovoltaic properties for solar semiconductor devices, such as cells and light emitting diodes. Here we implement a first principle study to identify and analyze dependence of optoelectronic properties of Cesium Lead Bromide perovskite, CsPbBr3, on composition, quantum confinement, and surface morphology. The calculations include combination of ground state modeling by DFT and dynamics modeling of excited state. The dynamic of excited states is modeled via Redfield equation of motion for electronic degrees of freedom, parameterized by nonadiabatic couplings, i.e. response of electronic states to thermal dynamics of nuclei. Specifically, we model how dynamics of photoinduced electronic state at the surface of 2D quantum confined films of perovskite depends on presence or absence of different adsortbates and symmetry of exposed crystallographic surface. By analyzing dynamics of charge redistribution between inner area of thin film of the perovskite and surface defects we can identify the winner in the competition between radiative and nonradiative recombination pathways, and, thus, quantum yield of photoluminescence. The obtained results allow for theory-guided design of optimal morphology of 2D perovskite films for light emitting applications.

1:45 PM ES17.11.02
The Correlation of Ferroelasticity and Chemistry in CH3NH3PbI3 Twin Domains Yongtuo Liu1,2, Anton V. Ievlev1, Lian Collins1, Songkil Kim1, Benjamin Dougherty1, Malshid Ahmadi2, Stephen Jesse1, Scott T. Retterer1, Alex Belianinov1, Kai Xiao1, Bobby G. Sumpter1, Sergei V. Kalinin1, Bin Hu2 and Olga S. Ovchinnikova1; 1Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 3Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Hybrid organic-inorganic perovskites (HOIPs) have drawn significant attention due to their extraordinary optoelectronic performance. Recently, two-dimensional structure was demonstrated that the films exhibit enhanced thermal/moisture tolerance under compressive strain and lower tolerance under tensile strain by physically bending the substrates. Here, we follow the evolution of stresses and highlight the thermal effects and structural changes in the film. For doing so, we also propose a processing method to achieve flat films with different stress states on transparent-conducting flexible substrates. The effect of residual stress on the optoelectronic properties and thermal and environmental stability of the films is studied. The observed changes in the film properties are correlated with the nature of the defects generated/annihilated as the film passes through a bending cycle. Understanding the fundamental role of stresses on film properties would help in discovering ways to mitigate its detrimental effects and achieve a more robust technology.
precise engineering and systematic characterization of the functional heterostructure in all-inorganic halide perovskite nanowires. On one work, we show that the n-p junctions can be readily induced through a localized thermal-driven phase transition in a single-crystalline halide perovskite CsSnI₃ nanowire. This phenomenon undergoes a phase transition from a double chain yellow phase to an orthorhombic black phase. The formation energies of the cation and anion vacancies in these two phases are significantly different, which leads to n- and p-type electrical characteristics for yellow and black phases respectively. Interface formation between these two phases and directional interface propagation within a single NW are directly observed under cathodoluminescence microscopy. Further, we demonstrate the current rectifying behavior of the resulting n-p heterostructure originating from the distinctly different charge transport properties of these two phases. On the other hand, taking advantage of the soft and reconfigurable ionic lattice characteristics in halide perovskite materials, we design a CsPbBr₂CsPbCl₃ heterostructure nanowire that bridges the pre-patterned parallel Au electrodes, via a precisely controlled anion exchange approach. Quantitative correlation between halide ion ratios and photoluminescence emission wavelengths in halide perovskites allows us to visualize the halide ion migration across the heterostructure interface under electric fields. More interestingly, we show that the halide ion migration is heavily dependent on the bias polarity across the nanowire, leading to the field-induced halide ion migration rectification in this solid-state material. The present approaches to heterostructure formation could inspire the precise control over the design of functional heterostructures using halide perovskites as building blocks.

2:30 PM BREAK

3:00 PM ES17.11.05
Discovery of Halide Perovskites—Crystal Chemistry, Photoluminescence and Their Optoelectronic Applications

Zhiguo Xia; School of Materials Science and Engineering, University of Science and Technology Beijing (USTB), Beijing, China.

Recently, the appearance of halide perovskites has catalyzed an unprecedented revolution in the field of (opto)electronics with tunability in the crystal-structure dimensionality and chemical composition. Our group has previously proposed a unifying methodology for the discovery of new earth phosphors for LED applications by mineral-inspired prototype evolution and new phase construction via cosubstitution strategy, and many useful phosphors have been reported. Since it is a challenge to discover the counterparts for rare earth phosphor, our group firstly conducted the investigations on perovskite quantum dots represented by CsPbX₃ to target the improved quantum efficiency and enhanced stability, and they also demonstrated potential for liquid crystal display backlight application. Secondly, in the search of stable lead-free perovskites, hybrid perovskites or perovskites double have been utilized. This development has yielded heterovariant substitution or chemical unit cosubstitution proposed by our group in the phosphor studies. Our pioneer work on Cs₂AgInCl₅ crystals, as an example, focused on the structural design, crystal structure, and morphology related with solution-based crystal growth habit, band structure, optical properties, and the stability. This compound has now become the “star” materials in the luminescent perovskites. Finally, our recent work on the crystal chemistry and photoluminescence behavior of the new zero-dimensional (0D) or two-dimensional (2D) structures will be mainly addressed in this talk, moreover the Mn²⁺ or other ions doped perovskites, as well as the photoluminescence and optoelectronic applications will also be discussed.

References:

Ming Zhao, Hongxu Liao, Xinling Xin, Qinyuan Zhang, Quanlin Liu, Zhiguo Xia. Next-Generation Narrow-band Green-emitting RbLi(Li₂SiO₃)(Eu²⁺) Phosphor for Backlight Display Application, Advanced Materials, 2018, 30(38) 1802489.
Fei Li, Ying Liu, Hongliang Wang, Qian Zhang, Quanlin Liu, Zhiguo Xia, Postsynthetic Surface Trap Removal of CsPbX₃ (X = Cl, Br, I) Quantum Dots via ZnX₂-Hexane Solution toward Enhanced Luminiscence Quantum Yield, Chemistry of Materials, 2018, doi: 10.1021/acs.chemmater.8b03442.

3:15 PM ES17.11.06
Thin-Film Processing for Large-Scale Optoelectronic Applications

Luis K. Ono, Longhui Qiu, Zonghao Liu, Yan Jiang, Matthew R. Leyden, Sonia R. Raga, Mikas Remeika, Emilio J. Juarez-Perez, Zhiguo Xia, Hongshao Wang and Yating Bi; Energy Materials and Surface Sciences Unit (EMSS), Okinawa Institute of Science and Technology, Okinawa, Japan.

Lab scale (<0.1 cm²) metal halide perovskite solar cells were fabricated to achieve power conversion efficiencies (PCEs) comparable to several other photovoltaic technologies. However, development of up-scaling processes (>10 cm²) with high PCE and stability is important for moving forward this technology towards commercialization [1,2]. At OIST, a team of researchers in the Energy Materials and Surface Sciences Unit has been making concerted efforts to develop processes aiming at high PCE, high-throughput, and minimum batch-to-batch variation, and compatible with large-area perovskite solar cells and modules. In this talk, we will present our recent progress to use chemical vapor deposition CVD [3-6] to fabricate perovskite solar cells and light-emitting diodes [7]. Also, we will introduce a novel methylamine (CH₃NH₂) gas induced crystallization process [8-10], which provides valuable insight into the formation of perovskite films.

In the past few years, the hybrid lead perovskite materials are the megastar in photovoltaics research field and has grab enormous attention due to its excellent absorption coefficient, charge-transport properties and long carrier life time. This thus has enabled a wide range of optoelectronic applications, notably in high efficiency photovoltaics with power conversion efficiency exceeding 23%; and bright light-emitting diodes (LEDs), sensitive photo-detector. Very recently, perovskites have been recognized as promising semiconductor for solid-state radiation detectors due to their high radiation absorption cross-section enhanced by the presence of heavy ions, such as lead, cesium and halide etc. State-of-the-art solid-state X-ray detector utilize germanium and silicon that exhibits an excellent detectivity. However, such performance is only achievable under bulk volume of materials due to its low z number, whereas operation suffers from charge diffusion and drifting that is detrimental to the detector sensitivity. Therefore, perovskite-based semiconductor with high mobility-lifetime product, low defect density would be a novel candidate for X-ray detector.

Here, for the first time we demonstrate a thin film X-ray detector using a P-I-N diode fabricated with highly crystalline Ruddles-Popper layered Perovskites thin films. It features with ultra-low dark current and high X-ray induced photocurrent signal, greater than state-of-the-art silicon diode. Most impressively, using merely 200 nm active layer, we could detect high energy hard X-ray above 10 keV with on/off ratio over 10^3. We attribute such performance to be the superior crystallinity in layered perovskite that suppressed recombination induced dark current that thus enhance the X-ray detection sensitivity. Our demonstration holds promise for efficient high energy radiation detection such as X-ray and low energy Gamma-Ray, using thin film PIN junction configuration. Our findings also inform a new generation of highly efficient and low-cost X-ray detectors based on Ruddles-Popper Layered Perovskites thin film.

**3:45 PM ES17.11.08**
Enhancement of MAPbBr3 Nanoparticles on Stability and Photocatalysis with a Polynorepinephrine Shell

Yidi Wang and Bin Fei; The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Organic-inorganic hybrid methylammonium lead halide perovskite (MAPbX3, X= Cl, Br, I) is an emerging candidate of diverse fields, including the light emitting diode, solar cell, photodetector, and photocatalysis. Due to their low formation energy, MAPbX3 materials are sensitive to many factors, including polar solvents, moisture, light, and high temperature. To address this issue, a straightforward method, encapsulating MAPbX3 nanoparticles (NPs) with stable polymer-like shells is commonly reported. Meanwhile, the previously reported encapsulated MAPbX3 were limited to the macroscale, which makes it difficult to develop the applications requiring monodisperse particles with high uniformity. In this work, monodisperse MAPbBr3@poly(norepinephrine) (PNE) NPs were successfully prepared by reverse micelle method and in-situ polymerization. In the polymerization process, the MAPbBr3 NPs were encapsulated with the stable and thin layer of PNE homogeneously, maintaining the intrinsic crystalline structure and monodisperse morphology. Meanwhile, PNE shell bearing alkyl hydroxyl groups resulted in activated MAPbBr3 NPs with remarkable features in photocatalysis tests even after treatment with water. Our work not only proposes a novel approach to produce core-shell perovskite NPs on the single particle level but also enhances the stability and photocatalytic efficiency of pristine perovskite.

**4:00 PM ES17 SUMMARY AND OUTLOOK: TOWARDS NEXT FRONTIERS OF PEROVSKITE RESEARCH**

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**SYMPOSIUM ES18**

Frontiers in Organic Photovoltaics  
April 23 – April 26, 2019

Symposium Organizer  
Nicolas Blouin, Fei Huang, South China University of Technology  
Bumjoon Kim, Korea Advanced Institute of Science and Technology  
Barry Thompson, University of Southern California

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* Invited Paper

**SESSION ES18.01; Device Physics I**  
Session Chairs: Harald Ade and Barry Thompson  
Tuesday Morning, April 23, 2019  
PCC North, 100 Level, Room 131 C

**10:30 AM ES18.01.01**
Excitons and Exciton Confinement in Organic Heterojunctions

Stephen Forrest, Xiao Liu, Kan Ding and Yongxi Li; EECS and Physics, University of Michigan, ANN ARBOR, Michigan, United States.

Excitons play a central role in photogeneration in organic detectors and solar cells. The efficiency of the exciton dissociation process is directly related to molecular structure of the donor and acceptor molecules and the film morphology. In our work, we have focused on understanding the microscopic nature of these interactions in both fullerene and nonfullerene based junctions. We have developed quantum mechanical models coupled with molecular dynamics simulations to understand the role that morphology plays on the energy of the charge transfer state – i.e. the intermediate between exciton and free polaron – and ultimately its ability to generate free charge at a low expense of energy. We find that quantum confinement of the exciton by crystalline domains in dilute donor-acceptor blends can result in substantial energy shifts in the state, thereby impacting its binding energy. [1, 2] Further, we have developed models that quantitatively relate the energy loss in nonfullerene acceptors to the molecular structure itself. Ultimately, this understanding of exciton and CT state energetics has led to very high efficiency (>15%) organic solar cells, with prospects of reaching 20% in the not distant future.[3, 4] The models, experiments and implications of these findings will be discussed in my presentation. Finally, if there remains time, I will discuss confinement effects in novel quantum well structures comprising a combination of organic and inorganic semiconductors, including 2D solids.[5]

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In this contribution, we report on analysis of non-radiative losses of representative solution-processed bulk-heterojunction OSCs based on NFAs with some of them achieving a remarkably low non-radiative $V_{OC}$ loss of 0.20 V, which is beginning to align with the state-of-the-art solar technologies based on silicon, CIGS and perovskite solar cells.[4-7] Analysis on the non-radiative recombination losses with its relation to intrinsic material's photo-physical properties, e.g., absorption coefficient, stokes shift, the energy-levels, photoluminescence efficiency, as well as extrinsic thin film properties, e.g., energetic and structural disorders, will be presented.

References

[4] X. Du et al., to be submitted.
Efficient NIR Organic Bulk Heterojunction Solar Cells Using Nonfullerene Acceptors

Thuc-Quyen Nguyen; University of California, Santa Barbara, Santa Barbara, California, United States.

The field of non-fullerene organic solar cells (OSC) has experienced rapid development during the past few years, mainly driven by the development of novel non-fullerene acceptors and matching donor semiconductors with device efficiencies approaching 15%. However, organic solar cell material development has progressed via a trial-and-error approach with limited understanding of the materials’ structure–property relationships and the underlying device physics of non-fullerene devices. In addition, the availability of hundreds of donor and acceptor semiconductors creates a large pool of possible donor–acceptor combinations, which poses a daunting challenge for rationally screening material combinations. Resonant soft X-ray scattering (RSoXS) has proven to be a powerful technique to measure domain purity in OSC active layer blends. In polymer-fullerene systems, RSoXS has shown that higher average domain purity is generally correlated to device performance. A simple interpretation of RSoXS purity measurements is complicated by the consideration that real morphologies may be composed of three or more phases, with mixed amorphous regions in addition to relatively pure, aggregated donor and acceptor domains. Whilst charges are understood to migrate to the aggregated domains due to a favorable electronic landscape, these charges might be effectively trapped in aggregates if there is insufficient number of percolating pathways in the amorphous mixed regions. Conversely, if the mixed regions have a composition much beyond the percolation threshold or if the volume faction of the mixed regions is large, then recombination is enhanced. Therefore, understanding the role of domain purity over different length scales and controlling the mixed amorphous phase for maximum charge creation and minimum recombination remains a principal challenge for non-fullerene OSCs.

We will summarize several of our RSoXS studies that compare non-fullerene acceptor based organic solar cells having different primary chemical structures of the constituents and with significant processing variations. Our analysis suggests that mixed regions are often detrimental to good performance in these systems, typically having a pronounced negative impact on FF. Optimizing performance continues to be a delicate balance of competing factors and the volume fraction of the ideal morphology remains to be determined. However, the miscibility of blend components, which might be probed using near-edge X-ray absorption spectroscopy as a screening tool, can guide expectations of achievable phase purity and ultimately the achievable performance of the active layer.

References
recombination rates.[1] Recent work has produced the liquid crystalleld bisphenol-a-thiophene-phenol (BTR).[2] When blended with PC71BM, BQR-based devices can achieve a power conversion efficiency over 9%, a high fill factor (FF) of 0.7, and also maintain good performance with a thick active layer. To further understand the structure-property relationships that yield high performance in this blend, we compare detailed morphological characterization from X-ray scattering [3] and transmission electron microscopy with a rigorous electrical model to predict the performance of donor and acceptor materials. However, the performance of BQR-based devices has not been determined to produce reliable measurements of donor and acceptor material properties and to demonstrate any improvements in the active layer of the donor and acceptor materials, in particular, for the device structure, the morphology of the active layer plays a crucial role in determining the power conversion efficiency (PCE) of the device. Considerable research has demonstrated that the donor and acceptor phase-separated the active layer to achieve efficient exciton separation, carrier transport and collection. However, non-fullerene molecules have two-dimensional structure, its strong electronic coupling is only expected for molecules oriented with their π systems parallel to each other, leading to a weak driving force for nucleation. Moreover, non-fullerene molecules have large molecular volume, inhibiting the process of molecular diffusion, which is not benefit for the crystal growth process. As a result, the crystallization of non-fullerene molecules was suppressed, inhibiting the formation of interpenetrating networks. Herein, we regulated the crystallization dynamics to enhance the crystallinity of non-fullerene molecules, i.e., regulating the crystallization process of donor and acceptor to reduce the molecular volume and enhance molecular diffusion capability. Take P3HT-O-IDTBR blends for an example, due to the film-forming process the crystallization of donor and acceptor tend to occur simultaneously. It would reduce the π-π interaction between like molecules, thus lead to a high nucleation barrier, which is not benefit for obtaining a film with high crystallinity. Here, TCB is selected as cosolvent to modify the film-forming kinetics due to its selective solubility and high boiling point. As a result, the crystallization process of P3HT and O-IDTBR was separated, which increase the chance of π-π electronic coupling among donors and acceptors, resulting in high crystallinity for both P3HT and O-IDTBR. Another factor to influence the formation of interpenetrating networks is the molecular diffusion capability. For example, for PDBD-T-TITC blends, due to the competition between crystallization and phase separation, the polymer is prone to crystallize first, which inhibits the molecular diffusion of ITIC, resulting in weak crystallinity of ITIC. We proposed to change the crystallization sequence of donor and acceptor, i.e., ITIC crystallized first, then the polymer crystallized. Thus, molecular diffusion of ITIC could be improved without the confinement of polymer, leading to an enhanced crystallinity. The enhanced crystallinity of non-fullerene molecules is beneficial to the formation of interpenetrating network, which facilitates the electron transport and suppresses the bimolecular recombination. This work demonstrates that manipulation of crystallization sequence of donor and acceptor may be a key to further optimize the morphology of NF-OSCs.

Organic solar cells (OSC) have drawn much interest due to their apparent advantages including lightweight, low-cost production, semitransparency, flexibility and large-area manufacturing. In addition to the synthesis of donor and acceptor materials, interface engineering and device structure, the morphology of the active layer plays a crucial role in determining the power conversion efficiency (PCE) of the device. Considerable research has demonstrated that the donor and acceptor phase-separated the active layer to achieve efficient exciton separation, carrier transport and collection. However, non-fullerene molecules have two-dimensional structure, its strong electronic coupling is only expected for molecules oriented with their π systems parallel to each other, leading to a weak driving force for nucleation. Moreover, non-fullerene molecules have large molecular volume, inhibiting the process of molecular diffusion, which is not benefit for the crystal growth process. As a result, the crystallization of non-fullerene molecules was suppressed, inhibiting the formation of interpenetrating networks. Herein, we regulated the crystallization dynamics to enhance the crystallinity of non-fullerene molecules, i.e., regulating the crystallization process of donor and acceptor to reduce the molecular volume and enhance molecular diffusion capability. Take P3HT-O-IDTBR blends for an example, due to the film-forming process the crystallization of donor and acceptor tend to occur simultaneously. It would reduce the π-π interaction between like molecules, thus lead to a high nucleation barrier, which is not benefit for obtaining a film with high crystallinity. Here, TCB is selected as cosolvent to modify the film-forming kinetics due to its selective solubility and high boiling point. As a result, the crystallization process of P3HT and O-IDTBR was separated, which increase the chance of π-π electronic coupling among donors and acceptors, resulting in high crystallinity for both P3HT and O-IDTBR. Another factor to influence the formation of interpenetrating networks is the molecular diffusion capability. For example, for PDBD-T-TITC blends, due to the competition between crystallization and phase separation, the polymer is prone to crystallize first, which inhibits the molecular diffusion of ITIC, resulting in weak crystallinity of ITIC. We proposed to change the crystallization sequence of donor and acceptor, i.e., ITIC crystallized first, then the polymer crystallized. Thus, molecular diffusion of ITIC could be improved without the confinement of polymer, leading to an enhanced crystallinity. The enhanced crystallinity of non-fullerene molecules is beneficial to the formation of interpenetrating network, which facilitates the electron transport and suppresses the bimolecular recombination. This work demonstrates that manipulation of crystallization sequence of donor and acceptor may be a key to further optimize the morphology of NF-OSCs.

4:00 PM ES18.02.06 Novel 4D-STEM Characterization of Nanoscale Morphology and Molecular Ordering in Organic Photovoltaics Gabriel Calderon1, Letian Dou2 and Jinwoo Hwang1; 1Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio, United States; 2Chemical Engineering, Purdue University, West Lafayette, Indiana, United States.

We present the novel characterization of the morphology and molecular ordering at the nanoscale structure of organic photovoltaics (OPVs) using 4-dimensional scanning transmission electron microscopy (4D-STEM). 4D-STEM utilizes the new-generation fast pixelated STEM detector that enables fast acquisition of electron nanodiffraction patterns from the entire area of the OPV with oversampling. The fast acquisition rate of the new detector is the key to minimize the radiation damage and carbon contamination on the sample when combined with low electron dose and in situ annealing. Real space reconstruction of the nanodiffraction data based on the intensity fluctuation analysis can reveal the detailed spatial and orientation maps of the structure with unprecedented resolution and precision. The new information we can gain from this new approach includes (i) the size, orientation and volume fraction of each type of ordered domains, (ii) how different domains (e.g. donor and acceptor domains) are correlated in terms of their structure and orientation at the interface, and (iii) how processing conditions or doping affects the molecular ordering and morphology in detail. We will demonstrate the results acquired from polymer OPV systems, blended with fullerene or non-fullerene acceptors, and also from more recent high-performance ternary systems, and show how their nanoscale structure and morphology relate to the charge transport, photovoltaic properties, and mechanical stability of the films.

Miscibility and Mixed Domains in OPVs—Is the Ever-Evolving Story of the Role of Mixed Domains Converging to a Stable Structure-Function Paradigm? Harald Ade; North Carolina State University, Raleigh, North Carolina, United States.

Polymer solar cells (PSCs) are lead-free and can now be processed from relatively benign solvents with high efficiency of >14%. For many years, progress has relied mostly on intuition and trial-and-error approaches. For example, it was commonly known that fundamental molecular interactions must control the achievable PSC morphology, quantifying these interactions and predicting important transient and final device morphology parameter such as the composition of the mixed domains and their relation to performance remained unattainable for a long time. This presentation will review the history of this winding road, the lost tracks, the parallel paths, and some of the blind alley of the field to understand “miscibility” and the phase behavior of PSC blends. Recent progress indicates that we might converge on a coherent understanding of structure-function relationships and that computer simulations might help to screen materials combinations for their suitability of high performance system. In some cases, the amorphous-amorphous phase behavior of a range of fullerene- and NFA-based systems has been determined and the metastable miscibility gap (the phase boundary) could be parameterized and thus quantified by the temperature-dependent Flory-Huggins interaction parameter χ(T). This has allowed to clearly show that there are two regimes: i) low χ systems with shallow quenches, where the best performance is achieved when the mixed domains reach the miscibility limit, and ii) high χ systems with deep quenches/low miscibility were the mixed domains have to be quenched into a composition that is close to the percolation threshold for electron transport. The deep quenched systems are intrinsically unstable and further purification of the mixed domains often leads to burn-in degradation, although some highly vitrified systems have been discovered. We will review these developments and arguments and present some preliminary data that also hints that there might be a relationship between χ and the propensity for a system to vitrify and thus be stabilized.
Design and Synthesis of Small Molecule Electron Acceptors for High Performance Organic Solar Cells

Hongzheng Chen; Zhejiang Univ, Hangzhou, China.

Fullerene derivatives are dominantly used electron acceptors in organic solar cells (OSCs) for decades owing to their high electron mobility and fine phase separation. However, the drawbacks of fullerene derivatives, such as high cost, poor absorption, limited energy levels tunability and morphological instability, provide an opportunity for the development of non-fullerene electron acceptors. So far, numerous non-fullerene electron acceptors, especially small molecule electron acceptors, are designed and synthesized with outstanding performances recently. Among them, fused-ring electron acceptors are the most famous ones with good structural planarity and rigidity, which successfully boost the PCEs of OSCs over 14%. In this presentation, I will introduce couple of small electron acceptors with unfused ring cores. PCEs over 12% can be obtained for polymer solar cells based on the electron acceptors with unfused ring cores. A high PCE over 14% is delivered for tandem polymer solar cells based on the newly designed NIR photoresponsive fullerene-free acceptor.

Development of Non-Fullerene Electron Acceptors for Organic Solar Cells

Jain McCulloch1,2; KAUST Solar Center (KSC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2Imperial College London, London, United Kingdom.

Development of non-fullerene electron acceptors for organic solar cells

The power conversion efficiency (PCE) of single junction organic solar cells has increased significantly during the last decade and now approaching the threshold considered necessary for commercialisation. During this period, the structural diversity of semiconducting donor polymers for solar cells has increased dramatically, enabling accelerated development of bulk heterojunction (BHJ) organic solar cells based on polymer donor materials and molecular fullerene derivatives. However, both the fullerene, and the low bandgap polymers typically suffer from low absorption coefficients due to weak oscillator strength. Our approach is to use P3HT as a p-type hole acceptor, and design highly absorbing, low-bandgap n-type small molecules to replace fullerenes. These fullerene acceptors not only have weak absorption, but also poor tunability of absorption over the longer wavelengths of the solar spectrum; morphological instability in thin film blends over time; high synthetic costs and limited scope for synthetic control over electronic and structural properties. For these reasons, we have developed new, synthetically simple electron acceptor materials, based on rhodanine end groups, which have much larger absorption coefficients than fullerenes, coupled with high lying LUMO energy levels, to maximize cell voltages. In BHJ devices with P3HT donor polymer, the rhodanine molecules were demonstrated to outperform fullerenes. The highest performing P3HT devices have power conversion efficiencies approaching 8%, based on a ternary blend of two rhodanine acceptors. We also demonstrate performances of over 12% with one non-fullerene acceptor in combination with lower bandgap polymers, deposited from non-chlorinated solvents.

Photo-Stability of Organic Solar Cells—Fullerene vs Non-Fullerene Polymer Solar Cells

Nutifafa Y. Doumon1, Mikhail V. Dryzhov1, Felix V. Houard1, Jingjin Dong2, Panagiotsi Christodoulis3, Azadeh R. Chatri1, Vincent Le Corre1, Giuseppe Portale4 and Lambert Jan Anton Koster2; 1Photophysics and OptoElectronics, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands; 2Molecular Chemistry and New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Tapping energy from sunlight can be a sustainable way to meet the increasing world energy demand. Organic photovoltaics (OPVs) are a viable technology in this direction. For the technology to be marketable, issues of low efficiency, high instability and the short lifetime of organic solar cells (OSCs) must be addressed. Recently, the advent of non-fullerene acceptors (NFA) made it possible for OSCs to break the 10% efficiency barrier hardly attained by fullerene acceptors (FA). This is because of the interesting possibilities offered by this new class of acceptors which the FAs are bereft of, namely, the broad/strong absorption, the facile synthesis, the ease of tuning their properties and the apparent enhanced stability.[1] Thus, in the past five years more than hundreds of NFA with applications in the OPV field were synthesized, thus, allowing for a notable current record efficiency of above 14%[2-3] in single junction solar cells and 17.3%[4] in a multijunction solar cells. Hence, there is an impressive shift in interest towards the NFAs. However, there has been little work on the stability of this new type of materials and devices. More importantly, there is very little to no comparative work on the photo-stability of FA vs. NFA solar cells, to really ascertain the pros and cons of the two systems.

In this work, we show the photo-stability of solar cells based on two workhorse acceptors, in both conventional and inverted structure, namely ITIC (as NFA) and [70]PCBM (as FA) blended with either PBDB-T or PTB7-Th polymer. We find that either irrespective of the polymer, the cell structure, or the initial efficiency, the [70]PCBM devices are more photo-stable than the ITIC ones. This observation, however, opposes the generally assumed claim that NFA solar cells are more stable. Finally, we propose ternary blend (D:A:A) made of the PBDB-T polymer and the two acceptors as a path to making the solar cell devices more stable. These findings suggest that there is still work left to be done for OSCs to achieve an acceptable level of stability.

References:

Designing Highly Efficient Non-Fullerene Acceptors via Tuning the Intramolecular Charge Transfer Effect

Huileng Yao and Jianhui Hou; Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Over the last few years, the development of fullerenefree organic photovoltaic (OPV) cells have achieved great attention, and the power conversion efficiencies (PCEs) of small molecular acceptor-based OPV devices have surpassed 14% recently. The non-fullerene small molecules have the advantage of easily tuned absorption spectra and molecular energy levels, contributing greatly to the rapid increasing PCEs of the resulting OPV devices. Among the varied kinds of non-fullerene acceptors, the ones with acceptor-donor-acceptor structures like ITIC show the outstanding performance. In our work, we tuned the intramolecular charge transfer (ICT) effect in this kind of molecules and designed a series of highly efficient materials.

First, we weakened the ICT effect of ITIC by replacing its benzene terminal groups with thiophene units to synthesize the ITCC. Then, we further added methyl groups on thiophene rings to decrease the ICT effect to prepare the ITCC-m.[1] As thiophene rings and methyl groups have relatively electron-donating properties than benzene rings, the ICT effect in ITIC is weakened gradually in ITCC and ITCC-m. When compared to ITIC, the ITCC and ITCC-m show upshifted the lowest unoccupied molecular orbital (LUMO) levels and blue-shifted absorption spectra. In the OPV cells fabricated with a polymer PBDB-T as the donor material, the ITCC- and ITCC-m yielded much higher open-circuit voltages.

Then, we adopted the contrary molecular design strategy to enhance the ICT effect in the small molecular acceptors. Taking IEIC as an example, we introducing the electron-donating alkoxy groups and electron-withdrawing fluorine atoms on the donor and acceptor parts of IEIC, respectively, to synthesize the IEICO and IEICO-4F.[2-3] Both of the acceptors show much-redshifted absorption spectra and thus obtained considerable enhancement of short-circuit current densities in the resulting OPV cells. Recently, we used the chlorination to replace the fluorination to further enhance the ICT effect and synthesized the IEICO-4Cl, which has very weak absorption in the visible range.[4] When blending different donors, the colors of the blend films were changed accordingly. We selected three polymer donor with varied colors and fabricated the semi-transparent OPV devices, to really ascertain the pros and cons of the two systems.
devices, which showed very good photovoltaic performance. We also integrating the advantages of the wide bandgap and narrow bandgap acceptors to fabricate the double-junction OPV cells. For example, we used the ITCC-m and IEICO to fabricate the front and rear devices in the tandem cells, respectively, a high PCE of 13.8% was recorded. After that, we replaced the IEICO with IEICO-4F with broader absorption spectrum, the PCE approached to 15%.

In our recent work, in order to understand the efficient charge transfer mechanism in these non-fullerene-systems, we studied the distributions of the molecular electrostatic potential (ESP) of these molecules. As there is much difference in electronegativity on the different part of the non-fullerene molecules, the theoretical calculations suggest that most parts of this kind of acceptor have positive ESP values. By contrast, the polymer donors usually have negative ESP on the backbones. Therefore, we think the ESP difference will induce an intermolecular filed to assist the charge transfer between the donors and acceptors in the active layers.


9:30 AM *ES18.03.05
Fused-Ring Electron Acceptors for Organic Photovoltaics
Xiaowei Zhan; Peking University, Beijing, China.

We proposed a new concept termed “fused-ring electron acceptor (FREA)”, invented the star molecule ITIC, created a class of high-performance nonfullerene acceptors, and built up an ITIC kingdom. The ITIC family presents some advantages: 1) Their chemical structures are facile to tailor and synthesis is easy to scale up; 2) Their absorption and energy levels can be tuned and thus match with various high-performance electron donors; 3) Their crystallinity and film morphology can be tuned; 4) They exhibit strong and broad absorption, especially in the 700–1000 nm range, and can match with wide-bandgap donor materials to achieve complementary absorption; 5) They have high electron mobilities similar to those of fullerenes. Single-junction binary-blend organic solar cells (OSC) based on these FREAs exhibit power conversion efficiencies of >14%. Moreover, the FREAs-based OSCs exhibit good morphology stability and long device lifetime. Now FREAs invented by Zhan group are commercial available. Around 130 research groups have already utilized these FREAs to fabricate high-efficiency OSCs, which surpass fullerene acceptor counterparts.

References

10:00 AM BREAK

SESSION ES18.04: Device Physics II
Session Chairs: Dean DeLongchamp and Fei Huang
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 131 C

10:30 AM *ES18.04.01
Materials and Device Structures for Efficient Organic Solar Cells and Photodetectors
Karl Leo; Natalia Sergeeva, Tianyi Li, Jonas Kublitski and Andreas Hofacker; IAPP, TU Dresden, Dresden, Germany.

Organic materials and devices offer the possibility for a novel electronics realized by low-cost processing on flexible substrates. Despite their limited mobilities, organic materials excellent optoelectronic properties which allow devices with excellent performance in photovoltaic and photodetector applications. Also, devices based on organic materials can display surprisingly high stability if well encapsulated from water vapor and oxygen.

In this talk, we will first present studies about the influence of defect states. We investigate defects in a system composed of the small-molecule oligothiophene derivative DCVST-Me blended with C-60, having power conversion efficiencies above 8% when used in a solar cell. Impedance spectroscopy shows a Gaussian distribution of trap states below the electron transport level. Comparison with drift-diffusion simulations show that the trap states mainly lead to a decrease of fill factor. Further, we discuss some new materials for solar cells and photodetectors based on bulky and merocyanine dyes. In particular the former class allows excellent devices absorbing in the infrared spectral range with high stability.

11:00 AM ES18.04.02
Nature of Photogenerated Defects in Bulk Heterojunction OPVs
Joshua Wolanyk, Raghunandan B-Iyer, Ruth Shinar and Joseph Shinar; Iowa State University, Ames, Iowa, United States.

Intrinsic photodegradation of organic solar cells, particularly bulk heterojunction (BHJ), remains a key commercialization barrier. Two types of photogenerated defects in BHJ films and related systems have recently been explored via electron paramagnetic resonance (EPR): (a) deeply trapped holes and electrons in polyelectrolyte-fullerene assemblies [1] and (b) carbon dangling bonds (C DBs) [2]; the latter were involved in support of simulations [3,4]. In both cases, the generated EPR defect signature observed in
photodegraded films weakens over several days. This talk will present new results of broadly examined various donor/acceptor structures, including of BHJ blend films with a non-fullerene acceptor, to obtain a comprehensive understanding of photodegradation. Evidence for C DBs vs deeply trapped holes and electrons will be discussed, given that the defects are generated largely by blue/UV irradiation rather than longer wavelengths. This observation clearly supports C DB formation over deeply trapped charges. The role of “hot” polarons in donor/acceptor interface C DB formation will also be discussed.


11:15 AM ESI18.04.03 Voltage Loss in Polymer Solar Cells and Perovskite Solar Cells Hyungdo Kim and Hideo Ohkita; Department of Polymer Chemistry, Kyoto Univ., Kyoto, Japan.

Solution-processed polymer solar cells and perovskite solar cells are a promising class of photovoltaic devices because of noticeable progress in the device performance with their many advantages such as flexibility and easy fabrication with low cost. The power conversion efficiency (PCE) has gradually increased over the last few decades and recently exceeded 14% for polymer solar cells. On the other hand, it has been steeply improved up to 23% for perovskite solar cells. In other words, the PCE of polymer solar cells still lag far behind that of perovskite counterparts. This is mainly ascribed to the difference in voltage loss (photon energy loss, \(E_{\text{loss}} = \mathcal{E}_p - qV_{\text{OC}}\)) between the two devices. The \(E_{\text{loss}}\) is typically in the range of about 0.7–1.1 eV for polymer solar cells while it is reported to be about 0.4–0.5 eV for perovskite solar cells. This indicates that such a voltage loss is dependent upon different mechanisms. In this research, we therefore studied the origin of \(E_{\text{loss}}\) in both polymer solar cells and perovskite solar cells. By measuring the temperature dependence of \(V_{\text{OC}}\), we discussed the difference in \(E_{\text{loss}}\) between the two devices. As a result, we found that there are temperature-independent and -dependent voltage losses in polymer solar cells whereas there is only a temperature-dependent voltage loss in perovskite solar cells. This discrepancy results from different charge generation and recombination mechanisms between them. On the basis of these experimental data, we further discuss the potential strategies for further improvement in \(V_{\text{OC}}\) for both devices.

References

11:30 AM ESI18.04.04 Quantifying Tie-Chain Fraction and Its Impact on Charge Transport in Model Conjugated Polymers Yueh-Lin (Lynn) Loo; Andlinger Center for Energy and the Environment, Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, United States.

The presence of tie chains that connect between crystallites can critically impact the electrical properties of conjugated polymers. Yet, the community has not yet been able to directly visualize them, let alone quantify their content in conjugated polymers. We applied the Huang-Brown model, a framework commonly used to elucidate the structural origins of mechanical properties in polyolefins, to quantify the tie-chain contribution to charge transport in a series of model poly(3-hexylthiophene), PSHT, and its blends. Plotting field-effect mobility as a function of tie-chain content, as extracted from the Huang-Brown model, collapses the data on a single curve not previously seen when the charge transport property is plotted against molar mass. We find a threshold tie-chain fraction of 10\(^{-6}\), below which intercrystallite connectivity limits macroscopic charge transport. X-ray paracrystallinity analysis of these PSHT films suggests intracrystallite disorder to be the bottleneck that limits charge transport when crystallitles are connected. Our study affirms the importance of connectivity between crystalline domains, with the Huang-Brown model implicating long polymer chains with rigid backbone to facilitate macroscopic charge transport.

1:30 PM ESI18.05.01 Molecular Design, Morphological Control and Device Characterization of Non-Fullerene Solar Cells with Significantly Reduced Photovoltage Loss and Enhanced Power Conversion Efficiency Alex Jen 1,2, 3; 1Department of Materials Science and Engineering, University of Washington, Seattle, Washington, United States; 2Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

Minimizing energy loss is a key aspect to transcend the current limitations on the performance of organic photovoltaics (OPV). However, an inherent limit has set for both devices.

2:00 PM ESI18.05.02 B—NContaining N-Type Conjugated Polymers and Polyarenes Chundong Dou, Jun Liu and Lixiang Wang; Changchun Institute of Applied Chemistry, CAS, Changchun, China.

Conjugated polymers and molecules are very important for their applications as semiconducting materials in organic electronics. In comparison to many p-type semiconductors, n-type semiconductors are very rare. Most of molecular designs of n-type semiconductors are based on the amide units. It is important but challenging to develop new design concept of n-type semiconductors. Based on organoboron chemistry,1,2 we now use boron-nitrogen coordination bond (B←N) as a powerful strategy to develop n-type semiconductors.3,4 We have proposed two approaches to design n-type conjugated polymers using B—N unit. The one is to replace a C−C unit by a B←N unit in conjugated polymers to transform a p-type polymer to a n-type polymer.4 The other approach is to construct novel electron-deficient building block based on B—N unit for n-type polymer.5 Following these two approaches, polymer electron acceptors containing B—N unit have been developed for all-polymer solar cells with power conversion efficiency of exceeding 8%.6 Moreover, we use B—N unit to design n-type polyarenes. A series of polyarenes containing B—N unit have been developed. They exhibit low-lying LUMO energy levels and high electron affinity. They have been used as electron-transporting semiconductors for solution-processed organic thin-film transistors. The electron mobility has reached 0.21 cm\(^2\) V\(^{-1}\) s\(^{-1}\). These results indicate that organoboron chemistry is a new toolbox to develop organic and polymer semiconductors.

Reference
The ability to control the translation of molecular properties to bulk properties remains crucial in our development of high performance materials for organic electronics. We investigate the effect of differing core substituents on the benzodithiophene-based high-performing organic photovoltaic (OPV) material BTR. Through sidechain engineering four novel p-type small-molecule semiconducting materials based on the BTR molecular structure are designed and synthesized to carry out this study, with one of our analogues possessing an excellent PCE of over 9% in simple device architectures. Through grazing incidence wide-angle X-ray scattering (GIWAXS) depth-dependent studies we find that this efficiency is realized through an optimal active-layer morphology comprised of a spectrum of crystallite orientations. We go on to establish that high solubility in the spin-coating solution during OPV active layer formation significantly improves the formation of this beneficial crystallite orientation. These results further our understanding of these high-performing class of materials and demonstrate the vital importance of solubility considerations to OPV morphology.

References:

calculate the properties of hundreds to thousands of co-polymers and as such generates sufficient data to train a deep neural network (DNN). This DNN can subsequently predict the properties of hundreds thousands to millions of co-polymers in a near instant. In our contribution we will briefly highlight the underlying machinery and discuss its predictions, both in terms of the general features of property space and co-polymers with particularly desirable properties for photovoltaics, for ordered binary co-polymers.


4:45 PM ES18.06.05
Non-Adiabatic Molecular Dynamics Study on Charge Transfer Dynamics at the Boron Subphthalocyanine Chloride/C60 Interface

Kosuke Satō, Ekadashi Pradhan, Kosuke Sato, Ekadashi Pradhan, Kosuke Sato, Senku Tanaka, Takuya Yoshitomi and Masaki Tsuka; Kindai University, Higashiosaka, Osaka, Japan.

We fabricated a semi-transparent organic photovoltaic (OPV) using a carbon nanotube (CNT) sheet as the top transparent electrode and an indium tin oxide (ITO) as the bottom electrode. A bulk heterojunction layer of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) was used as the photovoltaic layer. We investigated the illumination direction dependence on the photovoltaic properties of OPVs. It was found that the power conversion efficiency under the CNT side illumination showed the lower value than that under the ITO side illumination. Especially, the short-circuit current density (JSC) was decreased significantly.

A simple reason for the asymmetric photovoltaic properties was considered as the difference between the transparency of the two electrodes. The transparency of the ITO electrode (including the glass substrate) was higher than that of the CNT-sheet electrode. However, the decrease ratio of the JSC was much larger than the difference of the transparencies. In addition, the external quantum efficiency (EQE) spectrum of the CNT side illumination showed a decrease of EQE in the absorption region of PCBM. These results inferred that there were other reasons for the asymmetry.

To investigate the origin of the asymmetry, we fabricated semi-transparent OPVs with a wide range of thickness of the photovoltaic layer (50 ~ 5000 nm) and investigated the illumination direction dependence of the photovoltaic properties. It was found that the discrepancy of the JSC between the ITO side and the CNT side was increased with the increase of thickness. In the present OPV, electrons and holes were extracted from the ITO electrode and the CNT electrode, respectively. Hence, the difference of the illumination direction results in the difference of the transfer distance of electrons and holes.

We considered that a difference between electron and hole for an annihilation probability during the transfer through the bulk heterojunction layer was the main reason for the asymmetric JSC. We estimated an effective extraction length (EEL) of each carrier from the thickness dependence of the asymmetric ratio of JSC. Our results indicated that the EEL of electron was shorter than that of hole. It should be noted that, in many reports, the electron mobility in the P3HT:PCBM blend film is higher than the hole mobility: the trend of mobility does not explain our results. We consider that the EEL is another useful index for the understanding of the photovoltaic mechanism in the bulk heterojunction layer.

ES18.07.02
Doping ZnO Electron Transport Layers with MoS2 Nanosheets Enhances the Efficiency of Polymer Solar Cells

Renee Lee, Yi-Jiun Huang, Ben Chang and Kung-Hwa Wei; Materials Science And Engineering, National Chiao Tung University, Hsinchu, Taiwan.

In this study, we incorporated molybdenum disulfide (MoS2) nanosheets into solid-gel-processed zinc oxide (ZnO) to form ZnO:MoS2 composites for use as electron transport layers (ETLs) in inverted polymer solar cells featuring a binary blend active layer. We could effectively tune the energy band of the ZnO:MoS2 composite film from 4.45 to 4.22 eV by varying the content of MoS2 up to 0.5 wt%, such that the composite was suitable for use in bulk heterojunction photovoltaic devices based on poly[6,6]-phenyl C61 butyric acid methyl ester (PCBM). In particular, the power conversion efficiency (PCE) of the PTB7-Th:PCBM (1:1.5, w/w) device incorporating the ZnO:MoS2 (0.5 wt%) composite layer as the ETL was 10.1%, up from 8.8% for the corresponding device featuring ZnO alone as the ETL—a relative increase of 15%. Incorporating a small amount of MoS2 nanosheets into the ETL flattened the morphology of the ETL and resulted in enhanced fill factors and PCEs. We used ultraviolet photoelectron spectroscopy, synchrotron grazing-incidence wide-/small-angle X-ray scattering, atomic force microscopy, and transmission electron microscopy to characterize the energy band structures, internal structures, surface roughnesses, and morphologies, respectively, of the ZnO:MoS2 composite films.
Structural Isomerism as a Tool to Tune Properties in BODIPY Copolymers for Fullerene-Free Solar Cell

Gourav Tarafdar, Sanchita Sengupta, Upendra K. Pandey and Praveen C. Ramamurthy

1Interdisciplinary Center for Energy Research, Indian Institute of Science, Bangalore, India; 2Materials Engineering, Indian Institute of Science, Bangalore, India; 3Chemical Sciences, Indian Institute of Science Education and Research, Mohali, India.

Substituting fullerenes in organic bulk heterojunction (BHJ) solar cells with organic small molecules or polymers as electron acceptor can improve performances in solar cells. A lot of research is therefore being designed to test novel organic acceptors. Copolymers of 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene or BODIPY have been reported for photovoltaic applications. However, to our best knowledge in most of these reports the BODIPY copolymers have been used as the donor material in BHJ and the application of this class of materials as electron acceptor in organic BHJ solar cells have not been explored.

In this work we have synthesized four (two pairs) donor-acceptor copolymers of BODIPY with Benzodithiophene (P1 and P2) and Fluorene (P3 and P4). Each pair of polymers exhibit structural isomerism of the polymer backbone due to the difference in the point of attachment on the BODIPY (α or β) to the donor moiety (Benzodithiophene or fluorene).

The polymers are synthesized using Stille and Suzuki coupling reactions. The α connected polymers (P1 and P3) have a coiled backbone as compared to the β connected polymers (P2 and P4). The backbone isomerism is seen to alter the HOMO and LUMO energy levels of the polymer. While all the polymers have low lying HOMO (~ –5.2 eV) and hence good ambient stability, the energy of the HOMO in the aconnected polymers is than that in their bconnected counterparts. The polymers show narrow band gap (~ 1.5 eV) and absorption ranging from 700 nm to 900 nm which is influenced by the structural isomerism. The thermal stability of the a connected polymers (P1 and P3) is better than the β connected ones (P2 and P4). Space charge limited current (SCLC) measurements were performed to obtain the charge carrier mobility values in the polymers. Interestingly, the isomerism of the polymer backbone has no significant effect on the charge transport property of the polymers. All of the polymers exhibit ambipolar charge transport property with mobility values of the order of 10^-6 cm^2/Vs for the BODIPY-Benzodithiophene polymers and 10^-5 cm^2/Vs for the BODIPY Fluorene polymers. Photoluminescence quenching experiments on blend of these polymers with P3HT provide evidence of photoinduced charge transport from P3HT to these polymers. However, it was observed from Time resolved photoluminescence (TRPL) studies that charge transport is more efficient in the case of the α connected polymers than their β connected counterparts. This observation is supported by results from Density functional theory calculations which show greater degree of delocalization of the LUMO orbitals in the α connected polymers, whereas in case of the β connected polymers are the LUMO orbitals are mostly localized on the BODIPY units.

The better electron acceptor property of the aconnected polymers translates into better photovoltaic properties of the all polymer solar cells fabricated using P3HT: αP3αs as compared to P3HT: αP2P4. The best efficiency of these polymer solar cells is ~ 0.3 %. The low photovoltaic conversion efficiencies can be attributed to the low charge carrier mobility and hence low Voc. Modifying the alkyl side chain on the backbone of the polymer might be instrumental in improving the charge carrier mobility. Nevertheless, this study provides a crucial insight into the effect of LUMO delocalization on the ability of a material to perform as an electron acceptor. These results could be used as roadmap to the design of BODIPY based novel electron acceptor for fullerene free solar cells.

A DOE to Determine Significant Process Design Parameters in OPVs (Iain Tracton, Soumya Gupta, Zhila Hooshang, Jordan McNaughton, Jeremy Cody and Chris Collison)

The polymers are synthesized using Stille and Suzuki coupling reactions. The α connected polymers (P1 and P2) have a coiled backbone as compared to the β connected polymers (P4). The backbone isomerism is seen to alter the HOMO and LUMO energy levels of the polymer. While all the polymers have low lying HOMO (~ –5.2 eV) and hence good ambient stability, the energy of the HOMO in the aconnected polymers is than that in their bconnected counterparts. The polymers show narrow band gap (~ 1.5 eV) and absorption ranging from 700 nm to 900 nm which is influenced by the structural isomerism. The thermal stability of the a connected polymers (P1 and P3) is better than the β connected ones (P2 and P4). Space charge limited current (SCLC) measurements were performed to obtain the charge carrier mobility values in the polymers. Interestingly, the isomerism of the polymer backbone has no significant effect on the charge transport property of the polymers. All of the polymers exhibit ambipolar charge transport property with mobility values of the order of 10^-6 cm^2/Vs for the BODIPY-Benzodithiophene polymers and 10^-5 cm^2/Vs for the BODIPY Fluorene polymers. Photoluminescence quenching experiments on blend of these polymers with P3HT provide evidence of photoinduced charge transport from P3HT to these polymers. However, it was observed from Time resolved photoluminescence (TRPL) studies that charge transport is more efficient in the case of the α connected polymers than their β connected counterparts. This observation is supported by results from Density functional theory calculations which show greater degree of delocalization of the LUMO orbitals in the α connected polymers, whereas in case of the β connected polymers are the LUMO orbitals are mostly localized on the BODIPY units.

The better electron acceptor property of the aconnected polymers translates into better photovoltaic properties of the all polymer solar cells fabricated using P3HT: αP3αs as compared to P3HT: αP2P4. The best efficiency of these polymer solar cells is ~ 0.3 %. The low photovoltaic conversion efficiencies can be attributed to the low charge carrier mobility and hence low Voc. Modifying the alkyl side chain on the backbone of the polymer might be instrumental in improving the charge carrier mobility. Nevertheless, this study provides a crucial insight into the effect of LUMO delocalization on the ability of a material to perform as an electron acceptor. These results could be used as roadmap to the design of BODIPY based novel electron acceptor for fullerene free solar cells.

A Study on Mechanical Properties of Semicrystalline N-Type Polymers via Controlling the Molecular Weight—The Importance of Critical Molecular Weight for Stretchable Organic Electronics (Joohyeong Choi, Wansun Kim, Taek-Soo Kim and Bumjoon Kim)

The polymers are synthesized using Stille and Suzuki coupling reactions. The α connected polymers (P1 and P2) have a coiled backbone as compared to the β connected polymers (P4). The backbone isomerism is seen to alter the HOMO and LUMO energy levels of the polymer. While all the polymers have low lying HOMO (~ –5.2 eV) and hence good ambient stability, the energy of the HOMO in the aconnected polymers is than that in their bconnected counterparts. The polymers show narrow band gap (~ 1.5 eV) and absorption ranging from 700 nm to 900 nm which is influenced by the structural isomerism. The thermal stability of the a connected polymers (P1 and P3) is better than the β connected ones (P2 and P4). Space charge limited current (SCLC) measurements were performed to obtain the charge carrier mobility values in the polymers. Interestingly, the isomerism of the polymer backbone has no significant effect on the charge transport property of the polymers. All of the polymers exhibit ambipolar charge transport property with mobility values of the order of 10^-6 cm^2/Vs for the BODIPY-Benzodithiophene polymers and 10^-5 cm^2/Vs for the BODIPY Fluorene polymers. Photoluminescence quenching experiments on blend of these polymers with P3HT provide evidence of photoinduced charge transport from P3HT to these polymers. However, it was observed from Time resolved photoluminescence (TRPL) studies that charge transport is more efficient in the case of the α connected polymers than their β connected counterparts. This observation is supported by results from Density functional theory calculations which show greater degree of delocalization of the LUMO orbitals in the α connected polymers, whereas in case of the β connected polymers are the LUMO orbitals are mostly localized on the BODIPY units.

The better electron acceptor property of the aconnected polymers translates into better photovoltaic properties of the all polymer solar cells fabricated using P3HT: αP3αs as compared to P3HT: αP2P4. The best efficiency of these polymer solar cells is ~ 0.3 %. The low photovoltaic conversion efficiencies can be attributed to the low charge carrier mobility and hence low Voc. Modifying the alkyl side chain on the backbone of the polymer might be instrumental in improving the charge carrier mobility. Nevertheless, this study provides a crucial insight into the effect of LUMO delocalization on the ability of a material to perform as an electron acceptor. These results could be used as roadmap to the design of BODIPY based novel electron acceptor for fullerene free solar cells.

Impact of Molecular Planarity of Acceptor–Donor–Acceptor-Type Small Molecules on Molecular Packing and Photovoltaic Properties (Sang Woo Kim, Joohyeong Choi, Yu Jeong Lee, Young Woong Lee, Chang Woo Koh, Yeran Lee, Min Je Kim, Kin Liao, Jeong Ho Cho, Bumjoon Kim and Han Young Woo)

In this work, we have investigated the intrinsic mechanical properties of naphthalene diimide (NDI) based n-type conjugated polymer, P(NDI2OD-T2) via controlling the number-average molecular weight (Mn), varying from low to very high Mn = 15, 20, 48, 103 and 163 kg mol^-1. While we observed the general increasing trend of tensile properties as a function of Mn, a sharp transition in the strain at fracture and toughness values was observed between 48 and 103 kg mol^-1 with an increase by a factor of 26 and 160, respectively. The critical molecular weight at which the fracture toughness is minimal is attributed to the presence of large fraction of amorphous regions including tie molecules and interchain entanglements, which can effectively dissipate a substantial strain energy. The molecular weight dependence of mechanical behavior coincide well with thermal, viscoelastic and microstructural and thin film morphological properties. Therefore, our work suggests design rule for n-type conjugated polymer having good compromise between mechanical reliability and electrical performance for producing highly flexible and stretchable electronics.

High Temperature Semiconducting Polymer Blends (Aristide Gummesson, Purdue University, West Lafayette, Indiana, United States.)

In this study, we designed and synthesized a new A-D-A type SMs with thiophene-phenylene based central donor unit (P3T4) and different acceptor terminal groups of dicyanovinylene (VCN) and dicyanoindenedione (INCN). The P3T4 central donor unit is designed to allow intramolecular non-covalent Coulomb interaction, which has the feature that the torsional angle is minimized to improve planarity. We investigated the influence of terminal end-groups on intramolecular packing and the resulting electrical and photovoltaic characteristics. A small change in the end-group structure of the SMs induces a significant variation in the torsional structures, molecular packing, and pristine/blend film morphology. P3T4-VCN displayed a highly planar conformation and strongly crystalline morphology even in the post treatments and did not exhibit noticeable morphological changes. Our results demonstrate the importance of the terminal end-group for the design of A-D-A type SMs and their sensitivity toward the post-processing treatments in optimizing their performance.
Although high temperature operation (i.e., beyond 150 Celsius) is of great interest for many electronics applications, it is fundamentally challenging to achieve stable carrier mobilities for organic semiconductors at elevated temperatures. We report a general strategy to make thermally-stable high-temperature semiconducting polymer blends, composed of interpenetrating semicrystalline conjugated polymers and high glass-transition temperature insulating matrices. When properly engineered, such polymer blends display a temperature-insensitive charge transport behavior with hole mobility exceeding 2.0 cm²/Vs across a wide temperature range from room temperature up to 220 Celsius in thin-film transistors.

ES18.07.09

Relating Molecular Morphology to Charge Transport Through Efficient Multi-Scale Techniques
Matthew L. Jones1, Alexander L. Ayzer2, Lei Fang3 and Eric Jankowski1; 1Mieron School of Materials Science and Engineering, Boise State University, Boise, Idaho, United States; 2Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California, United States; 3Department of Chemistry, Texas A&M University, College Station, Texas, United States.

Solution-processed organic semiconductors are a promising class of materials, as they have the potential to be more economically viable than conventional inorganic photovoltaic devices, where fast return-on-investment and scalable, inexpensive manufacturing are a priority. The self-assembled molecular morphology strongly affects device performance and unlimited candidate molecules and processing protocols make it challenging to identify which combinations lead to nanostructures that result in the most efficient devices. Efficiently elucidating the links between morphology and final device performance is therefore a critical prerequisite for the large-scale adoption of these materials.

We demonstrate an open-source, multi-scale computational pipeline, MorphCT, that seamlessly combines molecular dynamics, quantum chemical calculations, machine learning, and kinetic Monte Carlo simulations. MorphCT encompasses length-scales from angstroms to microns and time-scales from femtoseconds to microseconds, linking molecular morphologies to device properties with excellent experimental agreement. We evaluate both donor and acceptor molecules across several classes of semiconductor (perylenes, fullerences, ladder molecules, polymers, and block-copolymers) for computer-aided device simulations, while identifying optimal processing conditions for device performance. This information is expected to be useful to device manufacturers to help focus further research efforts and identify a set of design rules for producing the most efficient devices.

ES18.07.10

Photonicallly Manipulated Polymer Solar Cells to Enhance Their Performance by Spectral Upconversion Systems
Ha-Eun Cho1, Na-Kyung Lee1, Young Jin Song1, Seok-Ho Cho2 and Sung-Min Lee1; 1Kookmin University, Seoul, Korea (the Republic of); 2Chonnam National University, Chonnam, Korea (the Republic of).

Despite many alluring advantages of polymer solar cells (PSCs) including low-cost fabrication process and device flexibility, comparatively low efficiency of PSCs has been a main hurdle for their full commercialization. There have been huge impressive efforts to overcome this drawback by developing active materials with high internal quantum efficiency, designing layer arrangement for high open-circuit voltage, and applying optical nanostructures that can enhance the photon absorption. Recently, novel approach of employing the spectral upconversion medium underneath cells has been arising to enable additional absorption for the solar photons for energy below the bandgap of active materials. While successful demonstrations of photovoltaics with the upconversion systems have been made for silicon or III-V solar cells, attaining meaningful enhancement of the performance of polymer-based thin film solar cells by such upconversion system is still challenging, because a reflective metallic electrode that can substantially increase the optical path length inhibits the penetration of the below-bandgap photons for excitation of the upconversion medium behind the cells, as well as of consequently upconverted above-bandgap photons. Herein we report an alternative design of PSCs to achieve the maximum benefits from the upconversion process without compromising pre-existing absorption of the incident solar photons. An opaque thick (~100 nm) silver (Ag) cathode typically used in PSCs is replaced by a multilayer electrode consisting of Ag (20 nm)/NPB (220 nm)/Ag (20 nm)/MoO3 (100 nm) that can selectively transmit the photons with wavelengths corresponding to the excitation (~980 nm) or emission (~540 nm) of NaYF4:Er3+ upconversion luminophors, thereby provoking the upconversion process and retrieving the resulting upconverted photons. To incorporate the highly effective upconversion system, a separately prepared upconversion medium deposited on a plastically nanostructured plate is attached to the damaged PSCs by using a polymeric adhesive without physical or chemical damages. The optimally designed PSCs with the plastically enhanced upconversion medium present a boosted level of the short-circuit current, even compared to the typical PSCs.

ES18.07.11

Semi-Transparent Quaternary Organic Photovoltaics Using NIR-Sensitive 4-Terminal Tandem System
Joo-Han Kang, Minwoo Nam and Doo-Hyun Ko; Applied Chemistry, Kyung Hee University, Yongin, Korea (the Republic of).

Organic photovoltaics are attracting much attention because they have many advantages such as low cost production, simple manufacturing process, and being able to fabricate on a flexible substrate which can be applied to modern technology. Here we exhibit highly-efficient and transparent quaternary organic photovoltaics (Q-OPVs) in a 4-terminal (4-T) tandem system. This system shows wide-range absorption spectra and high efficiency enough to assist other PV modules. This feature is meaningful that it can be used as additional tool for enhancing currently installed solar panels so that it can open up for possibility of diverse commercial applications.

ES18.07.12

The Importance of Molecular Weight in Optimizing the Mechanical and Electrical Performance of All-Polymer Solar Cells
Nup Balar1, Jeremy Rech2, Reece Henry3, Long Ye3, Harald Ade3, Wei You2 and Brendan T. O’Connor1; 1Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, United States; 2Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 3Physics, North Carolina State University, Raleigh, North Carolina, United States.

As organic photovoltaic (OPV) devices reach efficiencies that make them attractive for commercial implementation, it is becoming increasingly important to understand the thermo-mechanical behavior of the active layers to ensure reliable operation. This is particularly important to exploit intrinsic mechanical advantages of polymers to make physically robust flexible solar cells. Currently, high efficiency OPV devices are typically processed by blending a donor polymer with a small-molecule acceptor. These polymer-small molecule films, however, often demonstrate poor mechanical behavior and are prone to fail due to the detrimental effect of the small molecules. All-polymer solar cells (all-PSCs) provide a promising alternative that can be thermally and mechanically robust. However, the mechanical behavior of all-polymer films is dependent upon a number of factors of the individual polymers and interactions between the polymers. Here, we present the mechanical behavior of two high performing all-PSCs consisting of PDTT-TS1:PPDIODT and PBNDT-FTAZ:PDND2OD-T2. We focus on the fracture energy, crack onset strain, and storage and loss moduli of the films, and explore how the film morphology, polymer ratios, and polymer molecular weights impact both mechanical behavior and device performance. We also compare these results to their polymer:fullerene counterparts. We show that the all-PSC active layers can have a number of mechanical advantages over polymer:fullerene films including greater ductility and toughness and discuss the key molecular and morphological features that govern thermo-mechanical behavior. For example, we show that for the PBNDT-FTAZ:PDND2OD-T2 system, increasing the molecular weight of each polymer leads to both improved power conversion efficiency and cohesive fracture energy resulting in high performance mechanically robust flexible solar cells.

ES18.07.13

Balancing Crystal Size in Small Molecule Non-Fullerene Solar Cells Through Fine-Tuning the Film-Forming Kinetics to Fabricate Interpenetrating Network
Liu Jiampang and Yanchun Han; Changchun Institute of Applied Chemistry, Changchun, China.

All small molecule non-fullerene solar cells (AS-NFSCs), based on the binary blend of small molecule donors (SMDs) and non-fullerene small molecule acceptors (NFAs), are of emerging interest due to various virtues over conventional polymer/fullerene devices including easily tunable energy levels, well-defined chemical structure, high purity, and stable batch quality. In addition to the synthesis of donor and acceptor materials, interface engineering and device structure, the morphology of the active layer plays a crucial role in determining the power conversion efficiency (PCE) of device. Considerable research has demonstrated that the donor and acceptor should form an interpenetrating network, comprising a pure donor and acceptor crystals of 10-20 nm domain size with large interfacial mixed phase, to guarantee efficient exciton separation, carrier transport and carrier collection. However, in comparison with the case of polymer/fullerene or polymer/polymer based solar cells, achieving bicontinuous phase structure in AS-NFSCs is very challenging due to narrower processing windows, since small molecules are more sensitive to casting conditions. Furthermore, the variation trend of crystallinity for donor and acceptor are prone to follow the same trend, which inhibited to form similar crystal size between donor and acceptor.

Herein, we proposed the balanced crystal size between donor and acceptor is an important prerequisite to construct the interpenetrating network for AS-NFSCs. Additionally, the independent control of crystallinity for donor and acceptor was also realized by tuning the solution state and film-forming kinetics. Here, BDTT-S-TR (S-TR) was selected as...
donor and ITIC was chosen as acceptor. Due to the large difference in crystal size between S-TR and ITIC in blend system, i.e. the crystal size of S-TR ($L_d$) is 16 nm and the crystal size of ITIC ($L_a$) is 0, the phase separation was dominated by the crystallization of S-TR, thus formed grain-like phase separation structure. In order to balance the crystal size between S-TR and ITIC, an enlarged $L_d$ ($9.2$ nm) was achieved. The large crystal size between S-TR and ITIC-induced formation of interpenetrating network. The optimized morphology facilitates the dissociation of exciton and suppresses the recombination of charge transport process, leading to an improved device performance. Our work raised the principle for how to optimize the morphology of AS-NFSCs, and also provided method to individually control crystallinity for donor and acceptor, which could extend the ideal pair of SMDs and NFAs.

ES18.07.14 Preparation of Conjugated Polymers for Solar Cell Applications Using Direct Arylation Polymerization (DArp) Robert M. Pankow and Barry C. Thompson; University of Southern California, Los Angeles, California, United States.

Direct arylation polymerization (DArp) has emerged as a viable alternative to conventional polymerizations, such as Stille and Suzuki-Miyaura polymerizations, for conjugated polymer synthesis. DArP utilizes C-H activation, circumventing the need for the functionalization of monomers with a transmetalating reagent, reducing the overall number of synthetic steps and associated chemical waste. Through extensive study, conditions have been realized that allow for the polymer products with undetectable levels of undesired couplings (donor-donor, acceptor-acceptor, or branching defects). The incorporation of polymers prepared using DArP into electronic devices, such as organic photovoltaic applications has remained limited, however. We report the preparation of a series of perfectly-alternating conjugated polymers incorporating the acceptor thiieno[3,4-c]pyrroloindene and various donors and their incorporation into polymer bulk-heterojunction (BHJ) solar cells. The focus was to discover conjugated polymers that can be synthesized from simple building-blocks and their structure-property relationships unraveled. The ary groups incorporated into the TPD copolymers include thiophene (BT), thiienothiophene (TT), thiylenevinylene-thiophene (TVT), and ethylenedioxythiophene (EDOT). The BT based copolymer was shown to have the highest performance with a short-circuit current ($J_s$) of 10.54 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.74 V, and a fill-factor (FF) of 0.61 affording a power conversion efficiency of 4.76% with PC$_{60}$BM as the acceptor and fabricated under ambient conditions. This methodology is then applied to the polymer, poly[(4,4'-bis(2-butyletheroxy)-[2,2'-bithiophene]-5,5'-diyl)-alt-(2,2'-bithiophene-5,5'-diyl)] (PDBCT), which is made of simple constructs and the structure can be easily modified through varying of various monomers to generate a library of polymer donors for BHJ solar cell applications using DArP.

ES18.07.16 Efficient Ternary Organic Solar Cells Near-IR Sensitized by Porphyrins Xiaobin Peng; South China University of Technology, Guangzhou, China.

Multi-components organic solar cells (OSCs) that use mixtures of light absorption materials have shown promising progress of elevating power conversion efficiency (PCE) of devices. Comparing to binary bulk heterojunction (BHJ) mixtures, ternary mixtures, the simplest system in multi-components systems, provide a larger parameter space to fine-tune light absorption, energy levels, and morphology, with the added benefits of forming cascading energy transfer ladders and providing multi-transporting channels for charge carriers. It is thus believed that ternary mixtures are ideal systems for single layer devices, which can also be implemented in tandem devices to further improve device performances. The most popular ternary blends use two donor materials and modified fullerene acceptor to address the technical challenges in light absorption, morphology, carrier mobility and energy level alignment. Extraordinary successes have been demonstrated in mid-band gap hosting polymer PBT7 and PBT7-Th based mixtures. However, the complimentary light absorption absorbing materials in these high-performance ternary BHJ ternary blends are wide band gap species, which can only serve the purpose of energetic and morphological improvement. Extending absorption to near-infrared (NIR) region is still challenging, leaving as a “bottleneck” in multi-components OSCs. It should also be noted that ternary blends have a much more complicated morphology comparing to binary counterparts, leaving this feature a key parameter to be optimized. It would be of high interest to develop new systems that have a stable morphology and can sustain compositional variations, which can thus be further implemented in large scaled manufacturing. We show herein efficient ternary mixtures that reaches PCE larger than 11%. A recent developed deep absorbing porphyrin small molecule (DPPEZnP-TEH) dopant plays a key role in near IR sensitization. PTB7 based polymers presents much higher ratio of NT unit, which can be integrated with a wide-bandgap electron-donating copolymer PBTA-BO to construct all-heterojunction ternary BHJ OSCs. Comparison to binary counterparts, this feature is a key parameter to be optimized. It would be of high importance to develop new systems that have a stable morphology and can sustain compositional variations, which can thus be further implemented in large scaled manufacturing. The composite film showed an absorption beyond 900 nm, making it a breakthrough in ternary OSC research.

ES18.07.17 Effect of Fluorine Substitution on Molecular Interaction and Performance in Organic Electronics In-Bok Kim1, Soo-Young Jang2, Yunseul Kim3, Dongseong Yang1, Yeonsu Cho1 and Dong-Yu Kim4;1 School of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); 2Research Institute for Solar and Sustainable Energies, Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Fluorine (F) substitution on conjugated polymers in polymer solar cells (PSCs) has a diverse influence of molecular properties and device performance. We synthesize a series of three D-A type conjugated polymers (PBT, PFBT and PDBFT) based on dithienothiophene and benzothiadiazole units with different numbers of F atoms to find the effect on F substitution by comparing the molecular interactions of the polymer in PSCs. In the UV-Vis absorption spectra, the pre-aggregation behavior of fluorinated polymers in o-DCB proves that polymers have strong intramolecular interactions even in solution state. Besides, more closely packed structures of F substitution polymers are observed in polymer:PC$_{60}$BM blends by GIXD which is beneficial for charge transport and ultimately, for current density (4.3, 13.0 and 14.5 mA cm$^{-2}$ for PBT, PFBT and PDBFT, respectively) and for the fill factor (0.41, 0.68 and 0.69 for PBT, PFBT and PDBFT, respectively) in PSCs. Consequently, the PCE of PSCs reached 7.3% without any additional treatment (annealing, solvent additive, etc) in the polymer containing di-fluorinated BT (PDBFT) which is much higher than non-fluorinated BT (PBT – 1%) and mono-fluorinated BT (PFBT – 6%).

ES18.07.18 Influence of Energy Level Offsets in Ternary Blend Organic Photovoltaics Sanket Samal, Pratyusha Das, Negan Kazerooni and Barry C. Thompson; University of Southern California, Los Angeles, California, United States.

Ternary solar cells have become an important architecture for organic solar cells in recent years. By adjusting the composition of the active layer, the open circuit voltage ($V_{oc}$) of the solar cell can be tuned across the composition range of the active layer. It was theoretically proposed that the maximum offset between HOMO/LUMO energies of synergistic donors/acceptors couldn't exceed 0.3 eV without pinning the $V_{oc}$. Recently it was demonstrated that, the ternary blend active layer containing poly[2,5-bis[3-tetradecylhexyl]thiophene]-2,5′-diyl] [poly(3,4-dihexylquinacridone)-alt-phenylenevinylene]-alt-[poly(3,4-dihexylquinacridone)] as donor and two fullerene based acceptors having an offset of 0.5 eV between their LUMO energies still result in solar cells exhibiting maximum energy offset ($V_{oc}$). Although this shows that 0.3 eV is not the limit, the maximum achievable energy offset is still unknown for $V_{oc}$. We tried to address the issue by using a pair of two random donors consisting of poly[3-(3-hexylthiophene)-co-3-hexylhexithiophene] (PH3T-co-3HET) and poly[3-(3-hexylthiophene)-co-3-hexyloxythiophene] (PH3T-co-3HOT). This specific system was used because previous studies showed that we can easily tune the HOMO levels of the respective polymers by varying the composition of the individual monomers and can achieve a maximum offset of 1.2 eV between HOMO levels of PH3T-co-3HET and PH3T-co-3HOT. We have studied the influence of polymer surface energy on polymer-polymer miscibility, and judiciously functionalized the polymers to ensure adequate mixing for alloy formation. The characterization of the ternary blends and solar cell performance will be discussed.

ES18.07.19 Overcoming Morphological and Efficiency Limit in All-Polymer Solar Cells by Designing Copolymers Containing naphto[1,2-c:5,6-c']bis[1,2,5]thiadiazole] moity Wei Yang; South China University of Technology, Guangzhou, China.

We designed and synthesized a series of narrow bandgap conjugated copolymers by combining two conjugated polymers with various molar ratios of naphthobis[1,2,5]thiadiazole (NT) unit. All-polymer solar cells (all-PSCs) based on the resulting ternary copolymers NT40 and N2200 exhibited an impressively high power conversion efficiency (PCE) over 8.0%, which obviously outperformed those of obtained from devices based on the N70/N7102/N2200 blended films. Detailed characterization of the morphology of the films revealed that the incorporation of the NT unit can improve n-p stacking and a degree of phase separation conducive to exciton diffusion and charge transport. It is interesting to note that the resulting copolymer NT95, which has much higher ratio of NT unit, can be integrated with a wide-bandgap electron-donating copolymer PBTB-BO to construct all
PSCs with N2200, which presents an impressively high PCE over 10%. The improved photovoltaic performance is attributable to the combined effects of the extended absorption profile, a favorable film morphology, and more efficient charge transfer. Of particular interest is that these ternary blend films were processed using a non-halogenated solvent, 2-methyltetrahydrofuran, which is promising for practical applications. These findings lend credence to the ternary approach as a facile and promising strategy for achieving high-performance all-PSCs.

**ES18.07.20**

New Fully Conjugated Block Copolymer Bearing Wide-Bandgap Donor and Narrow-Bandgap Acceptor Blocks — Application to Single Active Material Polymer Solar Cell Hyung J. Kim, Ji Hyung Lee, Chang Geun Park, Young Un Kim, Su Hong Park, Na Yeon Kwon, Min Ju Cho and Dong Hoon Choi; Korea University, Seoul, Korea (the Republic of).

All polymer solar cells (PSCs) have attracted a considerable attention owing to their advantages such as their film-forming properties and the mechanical stability of their active layers. However, the major disadvantages of polymer/polymer blend films include poor miscibility, difficulty in controlling crystallinity, nonuniform internal phase composition, and large-scale phase segregation, all of which adversely affect the performance of the final PSC device. To overcome these shortcomings, much effort is being expended to develop a single-component active layer in PSCs which exhibits several key advantages such as simplified devices, stable internal morphology, and efficient exciton diffusion, dissociation, charge transport rather than a binary blend active layer. To date, few studies on single active material polymer solar cell (SAMPSCs) have been reported and the development of SAM is needed for the realization of high-performance organic solar cells.

In this presentation, we introduced a very intriguing conjugated block copolymers (CBCs) containing a p-type oligomeric unit and an n-type oligomeric unit. CBC showed very broad complementary absorption owing to the wide band gap of the p-type block and the narrow band gap of the n-type block, and also showed complete PL quenching because of the formation of photoinduced inter- and intramolecular charge transfer states. A CBC-based SAMPSC exhibited an unusually high PCE of ~4.00 % and excellent shelf-life under ambient conditions compared with the PSC fabricated with the blend film composed of p/n-type blocks. This is the first study to report excellent shelf-life for a CBC-based SAMPSC under ambient conditions.

**ES18.07.21**

Novel Terpolymer with Broad Complementary Absorption and Robust Morphology for Highly Efficient All Polymer Solar Cells Young Un Kim, Aesun Kim, Su Hong Park, Hyung J. Kim, Choel Hun Jeong, Jiwon Yoon, Na Yeon Kwon, Min Ju Cho and Dong Hoon Choi; Korea University, Seoul, Korea (the Republic of).

Terpolymer is designed by introducing a third monomer into the binary D–A copolymer structure and has a various property such as the absorption wavelength range, molecular energy level, charge carrier mobility, and solubility can be precisely tailored, often leading to improvements in the carrier mobility and power conversion efficiency (PCE) via synergistic effects between the three monomers. In other words, the chemical structure and distinct properties of the conjugated polymers can be finely controlled by this strategy. In this presentation, terpolymer, Ter-3MTTPD was synthesized using 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b0]dithiophene as a donor and methyl thiophene-3-carboxylate (3MT) and 5-(2-ethylhexyl)4-H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) as acceptor units to investigate its fundamental properties. The absorption spectrum of Ter-3MTTPD was intriguingly observed to the spectrum obtained by simply adding the absorption spectra of copolymers, Co-3MT and Co-TPD. This resulted in efficient complementary absorption properties after mixing NDl-Se as n-type polymer with Ter-3MTTPD. In terms of morphology, a blend film of Ter-3MTTPD:NDl-Se exhibited a relatively smooth surface and fine internal morphology, and the BHJ-type all-polymer solar cell (all-PSC) based on it provided a maximum efficiency of 7.7 %. This was further supported by the results of time-resolved photoluminescence (TRPL) in Ter-3MTTPD:NDl-Se blend film states and also showed the excellent shelf-life (~1000 h) of the all-PSC at ambient conditions compared to the other two copolymers.

**ES18.07.22**

Efficient Semi-Transparent Organic Photovoltaics Using Quaternary Blends Jisu Shin, Minwoo Nam and Doo-Hyun Ko; Kyung Hee University, Suwon, Korea (the Republic of).

Recently, organic photovoltaics (OPVs) have been studied through vigorous efforts, resulting in the rapid improvement of photovoltaic characteristics. This development has led to further research into the applicability as well as the performance of OPVs. Semi-transparent OPVs (ST OPVs) could be applied in many fields such as a window and roof of vehicle. We herein developed highly efficient ST OPVs based on quaternary blends involving additional donor and non-fullerene acceptor in polymer:fullerene binary OPVs. The ST Q-OPVs with experimentally optimized composition ratio exhibited high power conversion efficiency (PCE) under any illumination environments, this feature can open up the possibility of versatile commercial applications.

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**SESSION ES18.08: Processing**

**Session Chairs: Bunjoon Kim and Hyn-Lap Yip**

**Thursday Morning, April 25, 2019**

PCC North, 100 Level, Room 131 C

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**8:00 AM ES18.08.01**

Multi-Layered Polymer Solar Cells Using Stamped Active Layers from Water Juyeong Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

The device performance of bulk heterojunction (BHJ) polymer solar cells is very sensitive to the blend film nanomorphology including phase separation, molecular orientation, and crystalline nature, which depends significantly on the manufacturing process conditions such as temperature, humidity, and types of solvents and processing additives used. Especially in large-areas required for commercialization, these difficulties in controlling the nanoscale morphologies of both phases may degrade the reproducibility of the devices. Such sensitivity to processing conditions can be alleviated easily in multilayer heterojunction structures because individual layer properties including thickness and crystalline nature can be independently controlled, thereby simplifying morphology optimization and improving device performance. However, the multilayer heterojunction structures could be limited to certain materials and solvents combinations because the top layer should be sequentially deposited from a semi-orthogonal solvent with respect to the bottom.

Recently, we reported a novel technique that can form large-scale organic thin films while keeping high-quality nanomorphology in a very short time based on a Marangoni flow. The film formed from the process can be easily stamped and transferred on various substrates, suggesting the multilayer heterojunction structure can be effectively formed with high performing nanomorphology though the process. To obtain insight in the parameters controlling the formation of multilayer heterojunction structure, we study a bilayer structured device stamped poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]-thiadiazole)] (PPD2FTB) donor film on top of poly[N,N'-bis(2-octyldodecyl)naphtalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) (PND2O2D-T2) acceptor film us the aforementioned technique. Morphology studies reveal that more ordered molecular packing with strong face-on stacking and partially penetrated PPD2FTB molecules into the pre-deposited PND2O2D-T2 layer upon the solvent vapor annealing (SVA) process. Lastly, we discuss factors that control orientations of polymer backbones, which have great impact on the performance of optoelectronic devices.


**8:30 AM ES18.08.02**

Evaluating Stability of Push-Pull Small Molecule Donors for Organic Photovoltaics Trung Nguyen1, Kristen Watts1, Bharati Neelamraju1, Michael Anderson1, Wade Braunecker2, Zbyaw Owczerczyk2, Bryon Larson2, Bertrand Tremolet de Villers2, Ross Larsen2, Jeanne Pemberton1 and Erin L. Ratcliff1; 1University of Arizona, Tucson, Arizona, United States; 2National Renewable Energy Laboratory, Golden, Colorado, United States.
High efficiency organic photovoltaic devices have relied on the development of new donor and acceptor materials to optimize opto-electronic properties and control charge-transfer rates. To date, the highest single-junction organic photovoltaic devices have demonstrated ~14% power conversion efficiencies using non-fullerene acceptor molecules and tandem devices with efficiencies ~17%. For both donors and acceptors, push-pull of the electron density between different parts of the molecule allows for facile tuning of the band gap for maximizing the absorption of the solar spectrum, while simultaneously altering the redox properties to control the open circuit voltage and maximizing the photo-generated excitons to free carrier dynamics for optimal short-circuit current. Of these, small molecule-based materials hold exceptional promise over polymeric systems, with reduced batch-to-batch variations, high open circuit voltages and higher hole mobilities. Yet small molecules have more confined electronic density, which could make the materials more susceptible to degradation effects.

This work focuses on the degradation chemistry of a class of small molecule donors inspired by benzodithiophene terthiophene cores (BDT-3T) with rhodanine end caps, which have demonstrated 9% efficiency in single junction devices and ~11% in ternary cells. Herein we show that the same opto-electronic properties can be achieved for three additional molecules by simply changing the end cap to benzoazolato-terthiophene, pyrrole, or barbituric acid functional groups. This allows us to evaluate the stability of the 3T-BDT core as well as the role of the stability of the different end groups, each of which has unique spectroscopic signatures. Time-dependent degradation is monitored using both UV-vis and FT-IR spectroscopies, with changes in transmission related to the CIE color coordinate system. Changes in frontier orbitals and electronic structure are monitored using a combination of laboratory and synchrotron-based photoelectron spectroscopies and correlated to density functional theory predictions of degradation products.

8:45 AM ES18.08.03

Strategy for Efficient Eco-Friendly Processable Polymer Solar Cells via Side Chain Engineering of Aqueous Soluble Fullerenes
Youngkown Kim, Junhyeong Choi, Changyeon Lee, Youngwoong Kim, Changkyun Kim, Thanh L. Nguyen, Bhjo Gautam, Kenan Gundogdu, Han Young Woo and Bumjoon Kim; KAIST, Daejeon, Korea (the Republic of); Korea University, Seoul, Korea (the Republic of); Fayetteville State University, Fayetteville, North Carolina, United States; North Carolina State University, Raleigh, North Carolina, United States.

We develop a new series of aqueous solvent-soluble fullerene derivatives and successfully fabricate polymer solar cells (PSCs) using only aqueous solvents, essential to adapt for industrial criteria. In order to optimize the processability of the fullerenes in aqueous solvents and the device performances, different fullerene mono-adducts were designed by introducing oligoethylene glycol (OEG) side-chains having different lengths and the number of branches. As the results, we achieve the power conversion efficiency (PCE) of 1.4% for the PSCs processed by aqueous solvent in air. Significantly, the new fullerene derivative showed the superior electron mobility (1.30 × 10⁻⁶ cm² V⁻¹ s⁻¹), which is three different order higher than that of the previously reported alcohol soluble fullerenes owing to our design of fullerene-adducts that produce efficient packing between the fullerenes while ensuring sufficient solubility in aqueous solvents. Femtosecond transient absorption spectroscopy revealed the acceptor side chain to markedly impact geminate and/or nongeminate charge recombination in the PSCs. In addition, optimizing side-chains of these fullerenes produced the well-intermixed blend morphology with aqueous solvent-soluble p-type polymers to provide hole and electron pathway. Our results provide important guidelines for the design of the electroactive materials for real human-benign fabrication of the PSCs and other organic-electronics.

9:00 AM ES18.08.04

Toward Solution-Processed High-Performance Large Area Polymer Solar Cells
Zhang Kai; State Key Laboratory of Luminous Materials and Devices, South China University of Technology, Guangzhou, China.

While the performance of laboratory-scale polymer solar cells (PSCs) continues to grow, there are still challenges on the way to realizing efficient module devices, such as the low compatibility of the thickness-sensitive interlayer and active layer with large area coating techniques, the tremendous power loss on enlarged electrode, the frequent need for toxic solvents and tedious optimization processes used during device fabrication.

To avoid some of these problems and achieve high-performance large area PSC modules, we carried out a series of studies. Firstly, we developed a simple and efficient approach for achieving a large area cathode interlayer with controlled thickness at the nanometer-scale using an electrostatic layer-by-layer self-assembly (eLbL) process. The eLbL films exhibited excellent cathode modification ability and can be integrated into the current large area device processing techniques. Then, we employed a newly developed strategy of creating conjugated polymer P3NF-2TNDI as the ETL and PEDOT:PSS as the HTL to construct the interconnection layer (ICL) for conventional tandem PSCs, in which the device short current density (Jsc) was largely suppressed to minimize the power loss on the electrode. And then, we developed a highly efficient thickness-insensitive PSCs based on PTB7-Th:PC70BM that processed with single-component green solvent 2-methylanilole, in which both junction thickness limitation and solvent toxicity issues are simultaneously addressed. 16 cm² and 93 cm² PSC with the doctor-blade coating with a state-of-the-art power conversion efficiency of 7.5% and 4.5% were obtained.

Lastly, we have developed highly efficient (12.9%) non-fullerene PSCs by using sequential bilayer deposition method from non-halogenated solvents. More importantly, bilayer structure devices show less dependence on the processing condition (e.g., D/A ratio, solvent, annealing and so on). Using this bilayer processing method, PSCs can be scaled up to a larger area (1 cm²) while maintaining a high performance of 11.4% using the doctor-blade coating technique. This method offers a truly compatible processing technique for printing large area PSC modules.

Reference
Polymer solar cells (PSC) boasting a range of advantages including low cost, light weight and superior mechanical properties represent an important family in the third-generation solar cells. In the past few years, a variety of non-fullerene small-molecule acceptors have been reported, which afforded outstanding solar cell performances and are proven competent for replacing fullerene derivatives as the acceptor materials. Compared to the small molecule-polymer blends, solar cells comprising all-polymer active layers presumably present more stable donor-acceptor phase separation morphology and thus potentially superior long-term stability. The bottleneck of further enhancing the power conversion efficiency (PCE) of all-PSCs currently lies with the performance of polymer acceptors. Thus far, the most extensively studied polymer acceptors are naphthalenediimide (NDI) polymers, and pertinent all-PSCs have achieved impressive PCEs up to over 10%. Another important type of polymer acceptors is perylenediimide (PDI) polymers. Compared to NDI polymers, more versatile synthetic methods and diverse chemical structures have been developed with PDI polymers, which allow for more convenient tuning of the electronic and morphology properties. Our group have endeavored to improve the performance of all-PSCs by designing new high-performance PDI polymer acceptors. Particularly, we reported the application of a PDI-vinylene polymer acceptor (PDI-V) in all-PSCs. With PTB7-Th as the donor, PCE of 7.57% was attained. More recently, we designed and synthesized a new polymer acceptor NDP-V, which was chemically modified from PDI-V and contained an enlarged polycyclic aromatic dicarboximide, namely naphthodiperylene diimide (NDP), as the main building block, and the PCE of all-PSC using this polymer acceptor was boosted to over 8.5%. More recently, as an effort to fine tune the phase separation morphology, the donor polymer structure was further modified by adding chlorine substituents in the backbone. Upon adding the new polymer as a co-c donor to form a ternary blend active layer, the best PCE of NDP-V based all-PSC was further improved to over 9%. Finally, since perylene and naphthalenedicarboximide polymers both bring about outstanding performance, we are currently trying to develop new acceptor polymers by further diversifying the composing aromatic dicarboximide units. A series of new polycyclic aromatic dicarboximide monomers have been designed and synthesized, which will be applied to preparing new polymer acceptors.

10:00 AM BREAK

SESSION ES18.09: Ternary OPV
Session Chairs: Martin Heeney and Barry Thompson
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 131 C

10:30 AM *ES18.09.01
Ternary-Blend Solar Cell, a Leading Strategy in Development of OPV Technology
Takebeh Ameri; Physical Chemistry, University of Munich (LMU), Munich, Germany.

The unique selling points of organic photovoltaics (OPVs), such as excellent light harvesting capability, freedom of form, color and transparency, environmental friendliness, easy scalability and lower manufacturing costs based on roll-to-roll printing methods, position this technology for the mobile power market, and this most properly reflects the state of the art in commercialization. An important milestone towards OPV commercialization has been surpassed by reaching a power conversion efficiency (PCE) of over 15%. To boost the performance, ternary blend organic solar cells represent one of the most dominant strategies that have been explored in the last decade. The outstanding advantage of ternary blends consists of maintaining the simplicity of the processing conditions used for single active layer devices. Moreover, all the optimization strategies developed for binary cells can be also effectively applied for ternary solar cells. In this elegant configuration, all three photovoltaic parameters (V_{OC}, J_{SC}, FF) can be tackled simultaneously or individually by optimizing the ratio between the three materials used in the photoactive layer. Promisingly, the ternary-blend strategy, in single junction as well as multi-junction solar cells, has further closed the gap between the organic and perovskite photovoltaic technologies, where OPV technology has significant advantages in terms of large-area processability and environmentally-friendly nature. In this presentation, we will discuss our achieved results in details for various prototype organic ternary systems with a central focus on the fundamental complexity of microstructure and charge transport mechanisms. Importantly, we will explain the key issues that result in modified recombination mechanisms and consequently improved FF and V_{OC} in high-efficiency ternary solar cells.

11:00 AM ES18.09.02
Strategy for Designing Ternary Solar Cells from Interfacial Energetic View
Chuanfei Wang, Xianjie Liu and Mats Fahlman; Linköping University, Linköping, Sweden.

So called ternary device structure is being deployed to overcome the limitation of the binary solar cells for energy conversion. One of the most important tasks during design and fabrication of organic devices is to determine the energy levels of the organic materials and understand the energy level alignment at the interfaces involving semiconducting molecules and polymers. Introducing the third component in the ternary device structure means that there will be more interfaces in the devices. Therefore, it is urgent to find a general strategy to design efficient ternary solar cells from interfacial energetic view to improve the performance. A correlation between CV-derived oxidation potentials with UPS-derived IP is obtained for organic semiconductor films typically used in organic solar cells, enabling complementarily use of these two techniques [Sol. RRL 2018, 2, 1800122]. In organic devices, energy level alignment at interface can be described by integer charge transfer (ICT) model. Based on energy-level diagrams obtained with the ICT model, we design ternary solar cells by adding non-fullerene acceptor to binary blends, demonstrating an unprecedented increase in V_{oc} beyond the binary reference values and a significant improvement of PCE, J_{sc} and thermal stability simultaneously. [Nano Energy, 2017, 27, 24]. Ternary solar cells with minimum voltage loss were also developed by combining two donor materials featuring complementary optical absorption and the same ionization potential and positive ICT energy, matching the fullerene acceptor’s negative ICT energy. This design concept is shown to enhance dissociation of all polymer donor and fullerene acceptor excitons and to suppress bimolecular and trap assisted recombination [Adv. Energy Mater. 2017, 6, 1700390].

11:15 AM ES18.09.03
Correlating Morphological Characterization of the Active Layer of Ternary Organic Solar Cells with Their Photovoltaic Performance
Ismail A. Ayhan and Enrique D. Gomez; Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Ternary organic solar cells (TOSCs), consisting of multiple donor or acceptor materials in one photoactive layer, recently have emerged as one of the most promising strategy for broadening the light absorption spectrum and enhancing the power conversion efficiency (PCE) of photovoltaic devices compared with traditional binary solar cells. To enable efficient separation, transport and collection of charges, the photoactive layer morphology plays a dominating role for high-performance OSCs because there are some critical challenging issues such as controlling the phase separation and domain size of the device components. We propose that differentiating all-three components from each other in the TOSCs by using advanced characterization techniques can lead to a better understanding on the phase behavior and improvement of the device performance. Here, we demonstrate high-efficiency OSCs by combining the organic semiconductor components complementing with each other, such as donors(D) (PFBT4T-2OD (C_{66}H_{4}F_{2}N_{2}S_{2}O), PTB7-Th (C_{47}H_{38}N_{6}S_{2}), PCDTBT (C_{47}H_{38}N_{6}S_{2}), ICBA (C_{60}), PC71BM (C_{60}H_{4}O_{2}), IDIC (C_{6}H_{14}N_{4}O_{3}S_{2}), O-IDTBR (C_{6}H_{14}N_{4}O_{3}S_{2}), and their photovoltaic properties and morphology modification were studied through optimizing processing parameters such as polymer concentration, D:A1:A2 ratio, and thermal annealing. The effect of these parameters on the structural, morphological, electrical and photovoltaic properties were systematically investigated by performing UV-Vis absorption, Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) and Energy-Filtered Transmission Electron Microscopy (EFTEM). This work shows ternary systems composed of morphologically compatible acceptors at their comparable loadings can achieve fibril-like nanostructure features resulting in improving phase separation, a remarkable high PCE (>10%), significant enhancement of short-circuit current due to broadening of the absorption spectrum, and the fill factor. We attribute that the high morphology compatibility of the ternary system can benefit to optimize electron/hole mobility and diminish recombination. This study reveals the correlation of the morphology characteristic with the device performance and offers new insight from the perspective of morphology modulation for constructing efficient TOSCs.

11:30 AM *ES18.09.04
Design and Synthesis of Multi-Functional Materials for Highly Efficient and Perovskite Solar Cells
Sung-Ho Jin1 and Hyung Woo Lee2; 1Pusan National University, Busan, Korea (the Republic of); 2Department of Nanoenergy Engineering, Pusan National University, Busan, Korea (the Republic of).

Bulk heterojunction polymer solar cells (BHJ PSCs) and all-polymer solar cells (BHJ all-PSCs) have received great amount of interest in organic electronic applications due to
their unique features such as flexibility, fine tuning of optoelectronic properties and large area application. Even though, the power conversion efficiency (PCE) of PSCs and all-PSCs reached high PCE of 13 and 10%, respectively, the study towards stability and green solvent processable π-conjugated polymers are limited. In this scenario, we have developed two new series of fluorous containing π-conjugated polymers (P1-P3) and (NAP-1 and NAP-2). Especially, the fluorinated alkoxyphenylene-based 2D π-conjugated polymers (P1-P3) owns good compatibility with n-type polymers in all-PSCs and delivered a maximum PCE of 7.3% for P2 based devices in inverted all-PSCs. The second series of alkoxyphenylene substituted benzodithiophene based 2D π-conjugated polymers NAP-1, NAP-2 which effectively foresee the usage of green solvents and delivered a maximum PCE of 8.3% for NAP-2 in conventional BHJ PSCs without any additional treatments. In addition, we designed and synthesized a new efficient solution processable electron injection layer (EIL) PO-TAZ based on 1,3,5-triazine moiety. The application of PO-TAZ as an EIL in inverted PSCs delivered a high PCE of 10% with enhanced device stability.

SESSION ES18.10: Advanced Performance and Design I
Session Chairs: Jung-Yong Lee and Barry Thompson
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 131 C

1:30 PM *ES18.10.01
Fully Stretchable Semiconducting Polymers—Concept, Development and Application to Solar Cells Taiho Park; Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Fully stretchable optoelectronics such as plastic solar cells and displays (e.g., light emitting diodes) have become a core issue in materials and engineering academia and industries. To realize such advanced technology, development of novel concepts in active materials including electrodes, transistors, photo-related organics and substrates should be accompanied with other skills Among them, organic-based transistors employing conducting polymers could be a good model to develop new logics. Various studies have attempted to enhance charge carrier transport by increasing crystallinity. However, these approaches are inevitably limited by the semicrystalline nature of conjugated polymers. Moreover, high-crystallinity conjugated polymers have proven inadequate for soft electronics applications because of their poor mechanical resilience. Herein, we demonstrate that π-π stacking can aid energy dissipation when the polymer film is subjected to strain; furthermore, the π-π stacking prevents the chains from irreversible sliding out of place due to the applied strain.

2:00 PM *ES18.10.02
Optical Design for Advanced Tandem and Semitransparent Polymer Solar Cells Hin-Lap Yip; South China University of Technology, Guangzhou, China.

Optical management is a powerful strategy to enhance the performance of polymer solar cells by maximizing the light harvesting property of the devices. The capability to use optical model to precisely predict the light propagation property and charge generation rate within the devices allows us to design optimal device architectures with improved performance and stability.1 Here I will discuss how to apply high throughputs optical model to rapidly screen more than 10M device structures in order to identify the very best device design for extremely high performance tandem and semitransparent polymer solar cells.2-4 In addition, a multiple-function semitransparent polymer solar cell with both heat insulation and power generation properties will also be highlighted.3

References

2:30 PM BREAK

SESSION ES18.11: Device Physics III
Session Chairs: Tayebeh Ameri and Fei Huang
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 131 C

3:00 PM *ES18.11.01
Flexible and Durable Perovskite Solar Cells Using Fullerences and Nanocarbon Materials Yutaka Matsuoka1, 2; 1The University of Tokyo, Tokyo, Japan; 2University of Science and Technology of China, Hefei, China.

Carbon nanotubes (CNTs) have excellent charge carrier transport property and facilitates high flexibility of organic solar cells devices. In order to realize the use of CNTs in solar cells, we need to consider quality and electronic property of CNTs. We employ CNT transparent films made from aerosol CNTs which can be produced with floating iron catalysts prepared by thermal deposition of sublimated ferrocene. To obtain high electronic property of CNTs, we investigated bromsted acid, Lewis acid, and electrophilic fullerences for electronics application. We report CNTs-electrode-based flexible organic and perovskite solar cells. With replacing metal or metal oxide electrodes by CNT transparent electrodes, 1) use of CNTs as hole injection layer to realize stable PSCs with less than 10% efficiency loss under more than 1000 h continuous illumination. Also, we will discuss the use of fullerences for improvement of performance in organic and perovskite solar cells. Topics will be 1) Use of C

References

3:30 PM ES18.11.02
Intrinsic Reverse Dark Current in Organic Photodetectors Jonas Kuhlbi1, Donato Spoltore2, Andreas Hofacker1, Hans Kleemann1, Koen Van Den Heuvel2 and Karl Leo1, 1IAPP - Integrated Center for Applied Physics and Photonic Materials, Technische Universität Dresden, Dresden, Germany; 2IMO-IMOMEC, Universiteit Hasselt, Diepenbeek, Belgium.
Light sensing and imaging represent an important important technological field, demanding the use of outstanding photodetectors (PDs). This means a low dark current and high responsivity, resulting in a low noise current and high detectivity. Currently used PDs in the visible and near infra-red spectral region are based on hard solid state materials, namely silicon and InGaAs alloys. While their performance is outstanding, they cannot provide flexible, low cost and lightweight devices and imagers. Organic semiconductors have been shown to be suitable for accomplishing these needs and have already successfully been applied in solar cells and light emitting diodes. However, organic PDs still lack a high detectivity, especially in the near-infrared which is mostly a consequence of their high dark currents ($J_d$) and noise currents at reverse bias voltages, where PDs usually operate.

Due to impurities and their disordered nature, trap and sub-gap states are often observed in organic materials. In this work, we investigate the generation of charge carriers through trap and charge-transfer (CT) states and their influence on $J_d$. When suppressing extrinsic shunt paths, we observe that $J_d$ follows a trend with the energies ($E_{CT}$) of the subgap CT states formed at the charge generating donor-acceptor interface. Low energy CT states result in a reduced effective gap, over which charge carriers are thermally excited, resulting in increased dark currents. Furthermore, in specific donor:acceptor blends, we find trap concentrations of around 10$^{17}$ cm$^{-3}$ with an energy of around 0.45 eV below the transport level of the acceptor material. We were able to vary the trap concentration by varying the donor concentration while keeping $E_{CT}$ constant and observe that $J_d$ increases with increasing trap concentration. Dark current-voltage characteristics were simulated by a drift-diffusion model. By including trap assisted generation (Shockley-Read-Hall like generation-recombination process), we show that the expected value of $J_d$ increases four orders of magnitude and rules the dark $J'$ characteristics, limiting the detectivity.

By using electron/hole blocking layers and optimizing the energetic stack in our devices, we were able to achieve dark currents as low as 500 pA/cm$^2$ at -1V, leading to on/off ration of 10$^4$. To the best of our knowledge, this value of dark current is among the best values reported in literature for organic devices. Moreover, our experimental findings point out to a physical process that might be present in several donor:acceptor structures, explaining the high $J_d$ commonly observed in OPDs.

3:45 PM ES18.11.03

The Impact of Short Range Quadruple Interactions on the Photophysics of Quinquaraines and the Measured Efficiency in their Small-Molecule Photovoltaic Devices. Chris Collins$^{1,2}$, Chenyu Zheng$^{1,2}$, Tyler Wiegand$^{1,2}$, Michael Mark$^3$, Frank C. Spano$^3$, Jeremy Cody$^4$ and David McCamant$^4$, $^1$School of Chemistry and Materials Science, Rochester Institute of Technology, Rochester, New York, United States; $^2$ Nanopower Research Laboratories, Rochester Institute of Technology, Rochester, New York, United States; $^3$ Microsystems Engineering, Rochester Institute of Technology, Rochester, New York, United States; $^4$ Department of Chemistry, University of Rochester, Rochester, New York, United States; $^5$ Department of Chemistry, Temple University, Philadelphia, Pennsylvania, United States.

Electronic coupling and intermolecular charge transfer interactions strongly influence the excited state properties for organic solids, which dictate the effectiveness of these materials in optoelectronic devices. Exciton coupling via long-range coulombic interaction is both theoretically and experimentally well demonstrated for many small molecule crystals. However, the spectroscopic properties of a variety of closely-packed push-pull dyes cannot be explained by established Frenkel exciton models. We will describe our theoretical work with quinquaraines, demonstrating how the quadrupoole-quadrupole interaction must be accounted for when the intermolecular pi-stacking distance is small (< 3-5 Å).

We present the results of subpicosecond transient absorption spectroscopy, which probes the excited state photophysics of an anilino-quinquarine, known for its successful use in the active layer of organic photovoltaic devices. Our samples are designed with a continuum of intermolecular separations from monomers in solution, through solid solution thin films, to the fully condensed phase, demonstrating the increasing contribution of short-range quadrupole interactions. We measure excited state kinetics that confirm species assignments. The experimental results are in excellent agreement with our theoretical modeling.

We further considered the interpretation of theory and excited state characterization with our measured efficiencies in relevant small molecule organic photovoltaic devices. The comprehensive explanation of device efficiencies and time-resolved excited state absorption spectroscopy with our excited state modeling leads us to focus on a far-reaching mechanistic bottleneck for molecular and polymeric bulk heterojunction devices. With the identification of such a bottleneck, we discuss significant predictions for improved materials research for optoelectronic devices in general.

4:00 PM ES18.11.04

On the Design of Organic Solar Cells for Integration with Greenhouses. Eshwar Ravishankar$^1$, Jennifer Swift$^2$, Yuan Xiong$^1$, Long Ye$^1$, Reese Henry$^1$, Jeremy Rech$^1$, Carole Sarazivt$^1$, Wei You$^1$, Harald Ade$^1$ and Brendan T. O’Connor$^1$, $^1$ North Carolina State University, Raleigh, North Carolina, United States; $^2$ University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Organic photovoltaics have several key advantages over other solar cell technologies that include the ability to tune absorption characteristics through material synthesis and device design, and the ability to make semitransparent devices with a broad range of transmittance across the solar spectrum. Exploiting these features may be the key to successful commercialization of this technology. One promising application is to integrate semitransparent organic solar cells with greenhouses. Greenhouses provide a controlled environment for plant growth that results in significant increases in yield while reducing water consumption compared to conventional farming. However, greenhouses typically require significantly more energy per kg of food produced. Reducing the need for external energy input has the potential to lower the cost of greenhouse-produced food, and enable production in a greater number of geographical locations. Given this desire, there has been interest in solar powered integrated greenhouses for over a decade. However, in many demonstrations the incorporation of traditional silicon-based solar panels has shown poor performance due to the complete shading by the opaque panels. Here, we discuss the opportunity provided by semitransparent organic solar cells. The semitransparent solar cell absorption spectrum can be tuned to complement the absorption of plants rather than compete for the same light. This results in an opportunity to generate power without hindering plant growth. As part of this presentation, we show how the incorporation of semitransparent organic solar cells into greenhouses impacts the plant growth, power produced, and overall energy balance of the greenhouse. We use detailed models determined optimized solar cell designs and deployment strategies for various greenhouse geographical locations across the US. Furthermore, we experimentally demonstrate the modified growth behavior of red leaf lettuce under various semitransparent solar cells. Among the results, we show that the right combination of bulk heterojunction materials results in similar fresh weight of red leaf lettuce over its complete growth cycle compared to plant growth without solar cell coverage, highlighting the potential of this application.

4:15 PM ES18.11.05

Two-Dimensional benzo[1,2-b:4,5-b']difuran-Based Conjugated Polymers for High Performance Polymer Solar Cells. Yong Zhang; Harbin Institute of Technology, Harbin, China.

Polymer solar cells (PSCs) have achieved the significant advancements in the past decade. The power conversion efficiencies (PCEs) have undergone a rapid increment to over 13% for binary PSCs and exceeded 14% for ternary PSCs with the rapid developments of new materials and continuous innovations of the device engineering. Especially, the design of new materials plays the decisive role in pursuing higher PCEs for PSCs. Among the newly emerged materials, the success of non-fullerene acceptors in PSCs in recent years has provided a great opportunity to pursue the promising photovoltaic performances for the practical applications. Currently, the PCEs of the fullerene-free PSCs have reached over 13%, which is comparable or even higher than its PC71BM-based counterparts.

Benzodifuran (BDF), a furan-based derivative, has recently received considerable attention in the developments of conjugated polymers for PSCs. Compared with BDT unit, the furan-based BDF possesses the advantages of i) more planar structure as the smaller oxygen size of furan unit; ii) the lower highest occupied molecular orbital (HOMO) energy level as the strong electron negativity of oxygen atom; iii) the denser π-π stacking behavior. In addition, the furan unit is also available from the biorenewable sources with the low cost. However, the spectroscopic properties of a variety of closely-packed push-pull dyes cannot be explained by established Frenkel exciton models. We will describe our assignments. The experimental results are in excellent agreement with our theoretical modeling.

By using electron/hole blocking layers and optimizing the energetic stack in our devices, we were able to achieve dark currents as low as 500 pA/cm$^2$ at -1V, leading to on/off ration of 10$^4$. To the best of our knowledge, this value of dark current is among the best values reported in literature for organic devices. Moreover, our experimental findings point out to a physical process that might be present in several donor:acceptor structures, explaining the high $J_d$ commonly observed in OPDs.

4:30 PM ES18.11.06

Organic photovoltaics (OPVs) offer several advantages over other solar energy technologies. The ability to solution-process OPVs presents an opportunity for highly scalable and cost-effective manufacturing. Despite this, significant research efforts focus on small area cells that are fabricated using techniques, such as spin coating, that are not amenable to scale-up. This talk will illustrate that the performance of photoactive layer materials in OPVs fabricated using spin coating is not a reliable measure of scale-up potential. Rather, the evaluation of a material’s performance using a scalable coating technique, such as slot-die coating, is crucial. Limitations in materials’ air stability, solids content, and solvent toxicity all present significant challenges to successful scale-up. This talk will highlight advances, such as the use of more air-stable non-fullerene electron acceptors and improvements in materials coating properties that have enabled the fabrication of ~300 nm thick photoactive layer films for 12 cm² OPV modules reaching 8% power conversion processed in air using scalable techniques.

4:45 PM *ES18.11.07
Surface Photovoltage Spectroscopy of Bulk Heterojunction and Dilute Donor Organic Photovoltaic Structures Lakshmi Narayanan Novel Saravana Murthy, Diego Barrera, Aakash Gadi, Liang Xie, Fong-Yi Cao, Cheng-Chun Tseng, Yen-Ju Cheng and Julia W. Hsu; The University of Texas at Dallas, Richardson, Texas, United States; Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

Organic photovoltaic (OPV) devices have attracted significant attention due to the low cost of fabrication, lightweight, and mechanical flexibility. Photogenerated charge transfer from active layer to carrier transport layer is critical for realizing efficient OPV devices. Defect states in the active layer or at the interface between active layer and charge transport layer can impede the charge transfer process by introducing traps, recombination centers, and limiting exciton diffusion. Here, we perform surface photovoltage spectroscopy (SPS) to study defect states in organic photovoltaic structures with different active layer systems. SPS measures surface photovoltage (SPV) as a function of incident photon energy, and has been used for obtaining electronic structure and electrostatically active defects of semiconductors. In SPS, sub-band illumination probes the transition between the band states and defect states within the bandgap. Here, we performed both steady-state (DC) and frequency-modulated (AC) SPS on bilayer structures containing different active layers (P3HT, P3HT:PCBM, PBFT:Se:Th:PC71:BM) and zinc oxide (ZnO) electron transport layer (ETL) to probe photogenerated transfer across this interface. AC SPS measures SPV signals of chopped monochromatic light at specific frequency. DC SPS measures stabilized SPV signals using continuous illumination from longer to shorter wavelengths. DC spectra are broader compared to AC spectra for all active layers. AC spectra overlaps with the absorption spectra of active layers, evident that AC SPS corresponds to band-to-band transitions. The sub-bandgap signals measured by DC SPS also include transitions with the bandgap states. When hole transport layer (HTL) was deposited on top of the active layer, the DC spectra are narrower than without the HTL, suggesting that the surface states are removed. In addition, we study DC SPS on dilute donor active layer (0.1, and 5wt% P3HT in PC71:BM) with conventional (on PEDOT) and inverted (on ZnO) architectures. We observed the positive SPV signal in the conventional structure, indicating that holes transferring to PEDOT and DC SPS magnitude increases with donor concentration. In the inverted structure, negative SPV signal indicates that electrons transferred to ZnO and DC SPS does not change with donor concentration due to the higher electron mobility of PC71:BM. These results give better insight on location and nature of sub-bandgap defects based on their SPS spectral signatures and frequency response.

SESSION ES18.12: Synthesis II
Session Chairs: Bumjoon Kim and Barry Thompson
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 131 C

8:00 AM *ES18.12.01
Developing High Performing Ladder-Type Materials for Organic Solar Cells Martin Heeney; Imperial College London, London, United Kingdom.

Ladder type fused aromatic monomers have been at the forefront of conjugated semiconductor development, finding use in both donor polymers and non-fullerene acceptors for high efficiency solar cell blends. Here we discuss recent efforts to develop flexible synthetic routes to a range of such monomers which allow the ready manipulation of the solubilizing sidechains, as well as the aromatic heterocycle in the fused unit. We show that the nature of the sidechain is important for both donor polymers, and non-fullerene acceptors. Changing from commonly used arylalkyl to simple alkyl sidechains is shown to have a positive impact on the performance of materials in single junction solar cells. The reasons behind these differences will be explored.

8:30 AM *ES18.12.02
Optimizing the Active Layers of High-Performance Organic Photovoltaic Cells Jianhui Hou and Shaoqing Zhang; Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Over the last three decades, organic photovoltaic (OPV) cells achieved much significant progress, and power conversion efficiencies (PCEs) of over 14% were recorded.1 The development of organic active materials including electron donors and electron acceptors, device engineering, and device physics contribute greatly to the rapid increase of PCEs. In our work, we prepared many conjugated polymers and used them to fabricate the OPV devices for better performance. In 2008, we first incorporated the benzodithiophene units into the designing of polymer donors and achieved very good results.2 Then we systematically studied this type of polymers and summarized some useful strategies to improve their photovoltaic performance. For example, we used the conjugated side chains to modify the BDT units to improve the charge transport properties. Based on this method, we reported some highly efficient polymer donors for OPV devices. In 2014, we fabricated the OPV devices with over 10% efficiency using the BDT-based polymer PBDB-T1 as an electron donor and PC71BM as an electron acceptor, which was among the top values in the OPV field.3 Over the last few years, the non-fullerene electron acceptors achieved much rapid progress. Many non-fullerene acceptors such as ITIC were reported, which showed very promising features in easily tuned optical absorption and molecular energy levels. We blended a BDT-polymer named PBDB-T with ITIC as active layers and first achieved over 10% efficiency for non-fullerene-based OPV cells.4 Then we further optimized the polymer donor and non-fullerene acceptor via introducing fluorene atoms on PBDB-T and ITIC, respectively.5 The resulting donor PBDB-T:SF and non-fullerene acceptor IT-4F showed synergistically down-shifted molecular energy levels. Interestingly, the newly prepared active layers had broad absorption spectra and higher absorption coefficient. Due to the considerable enhancement of short-circuit current densities, PCEs over 13% was obtained. In our recent work, we designed some small molecules and used them as solid additives to optimize the morphology of the active layers. The small molecular additives were designed to have similar chemical structures with the terminal groups of highly efficient non-fullerene acceptors, resulting in very good miscibility between them. Via the treatment of thermal annealing, the additive could volatilize from the active layer, and meanwhile, the intermolecular pi-pi stacking was enhanced greatly, which benefited the charge transport and led to better photovoltaic performance. Importantly, when we tested the OPV cells processed with some solvent additives with high boiling-point like DIO, the devices fabricated using volatilizable solid additives showed better device stability and reproducibility, which will benefit the largescale production of OPV cells.

References

9:00 AM ES18.12.03
Electron-Donating Conjugated Polymers Containing pyrrolo[3,4-f]benzotriazole-5,7-dione Unit for Polymer Solar Cells Lei Ying; Institute of Polymer Optoelectronic Materials and Devices, State Key Lab of Luminescent Materials and Devices, Guangzhou, China.
Based on a moderate electron-deficient 6-alkyl-2-alkyl-5H-pyrrolo[3,4-f]benzotriazole-5,7(6H)-dione (TzBI) as the building block, we developed a series of donor-acceptor type of wide bandgap conjugated polymers based on benzothiophene derivatives as the electron-donating moiety. The resulting copolymers exhibited remarkable solubility in non-chlorinated solvent, such as 2-methylethyltetrahydrofuran, which are benefited from the incorporated solubilizing alkyd side chains in both imide and triazole moieties. By finely tuning the molecular structures of PTzBI-derivatives and non-fullerene acceptors of ITIC derivatives, we achieved an impressively high certified power conversion efficiency (PCE) over 12% at a relatively large device area of 1.0 cm². By combining the donor and acceptor moieties, we demonstrate that Voc loss might be partially originated from a low but non-negligible charge transfer state. These findings highlight that the reduction of the bandgap to improve the efficiency requires a careful materials design to minimize non-radiative Voc losses. By incorporating siloxane substituents into the side chain of the PTzBI, we achieved PTzBI-Si that presents excellent solubility in non-chlorinated green solvents. The all-polymer solar cells constructed based on PTzBI-Si:N2200 gives a remarkable PCE of 10.1% and 11.2% for single junction and tandem all-polymer solar cells, respectively. Our results demonstrate the great potential of using PTzBI derivatives for constructing highly efficient polymer solar cells.

9:15 AM ES18.12.04
Pt-Containing Conjugated “Roller-Wheel”–Shaped Materials for Organic Photovoltaic (OPV) Applications Yang Qin; Department of Chemistry and Chemical Biology, The University of New Mexico, Albuquerque, New Mexico, United States.

Incorporation of transition metals into conjugated structures has been widely applied as an intriguing strategy to give organic materials with novel properties characteristic to metals. Among various transition metal complexes, those of Pt(II) are unique because they intrinsically adopt square planar geometries and can serve as building blocks for linear long-chain structures. These complexes typically show strong spin-orbit coupling effects that induce facile formation of long-lived triplet excitons, which have been considered beneficial for organic photovoltaic (OPV) operations. Consequently, Pt-containing conjugated polymers (CPs) have recently attracted significant attention in OPV research. A variety of CPs containing Pt(II)-bisacetylide building blocks have been prepared and studied in detail. However, except for a handful of examples showing reasonable device performances up to ca. 4% power conversion efficiencies (PCEs), most of the Pt-containing polymers performed very poorly.

We have devised a new structural design motif for Pt-bisacetylide containing materials, namely “roller-wheel” shaped molecules, in contrast to the “dumbbell” type geometries in traditional Pt-containing small molecules and polymers.1,3,4 We have prepared a series of such “roller-wheel” complexes having an identical Pt-containing core (the “wheel”) and different conjugated arms (the “roller”). It was revealed that if the “rollers” are long enough, these molecules can “slip-stack” in the solid state, leading to high crystallinity and charge mobility. OPV devices were fabricated and showed power conversion efficiencies up to 5.9%, out-performing all existing Pt-containing materials. These materials generate long-lived triplet excitons that are mostly dark and not converted to electricity in the current device setup. We thus applied transient absorption studies using different electron acceptors to estimate the triplet energy levels, which shed light on how to capture triplet excitons in OPV devices, a rarely investigated mechanism that can potentially improve device performance.


9:30 AM ES18.12.05
Design and Synthesis of Ladder-Type Organic Conjugated Materials for Organic Photovoltaics Yen-Ju Cheng; Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan.

Forced planarization by covalently fasting adjacent aromatic units in the conjugated backbone strengthens the parallel p-orbital interactions to elongate effective conjugation length and facilitate electron delocalization, providing an effective way to reduce the band gap and enhances the intrinsic charge mobility. It is envisaged that the well-defined ladder-type small molecules can function as donor monomers to polymerize with acceptor units, leading to a new class of donor-acceptor semi-ladder copolymers that can be suitably used for solution-processable polymer solar cells. Therefore, elegant designs and synthesis have been devoted towards hybridizing electron-rich aromatic subunits into mutually fused structures in the anticipation of extracting their individual intrinsic advantages. Various accessible electron-rich aromatic and heterocycles building blocks can be chemically assembled to afford a range of fascinating ladder-type conjugated skeletons with tunable properties and functions. A series of donor-acceptor conjugated copolymers have been designed and synthesized. On the other hand, the deformylated ladder-type building blocks can be further end-capped with two acceptors to form a new class of A-D-A small type molecules. These molecules can serve as n-type materials to replace traditional fullerene materials. By combining with the suitable p-type polymers to form complementary absorption and matchable energy levels, the devices using ladder-type-based nonfullerene acceptors have achieved high power conversion efficiencies. The applications of these materials in solar cells and OFET transistors will be discussed.

Reference

10:00 AM BREAK

SESSION ES18.13: Advanced Performance and Design II
Session Chairs: Fei Huang and Barry Thompson
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 131 C

10:30 AM ES18.13.01
Aqueous-Processable Organic Photovoltaic Materials for Green Energy Sources Han Young Woo; Korea University, Seoul, Korea (the Republic of).

Over the past few decades, organic solar cells (OSCs) have made a significant progress, showing their great potential for low-cost, flexible, lightweight, portable and large-area energy-harvesting devices. Although PC61BM and/or PC71BM structures have been exploited successfully in OSC devices, efforts to modify the fullerene structures for further improving the device performance have been tried recently because fullerene derivatives have the inflexibility in molecular design, difficult purification, poor morphological stability, and limited light absorption in the visible region, etc. In recent years, nonfullerene acceptors have emerged as an alternative candidate of n-type materials to overcome the difficulties of fullerene derivatives in tuning optical and electronic properties. The strong and easily adjustable absorption characteristics of nonfullerene acceptors have been considered as a strong point compared to fullerene-like structures, showing a photovoltaic efficiency over ~14%. To further optimize the OSCs for next generation green energy sources, several important points need to be considered carefully. Here we discuss the fundamental correlations between molecular structure, blend morphology and device performance in fullerene- and nonfullerene based PSCs. We will also discuss the indoor light harvesting, single component OSCs and aqueous-based eco- and human-friendly fabrication of OSCs in detail.

11:00 AM ES18.13.02

In the current research, organic photovoltaics (OPVs) with various annealing temperature of TIPS-pentacene between ZnO (Zinc Oxide) interface layer and active layer were
investigated for better current density. The TIPS-pentacene was dissolved in anisole overnight at room temperature, to give the blend solution for device fabrication and we prepared inverted bilayer electron transport layers (ETLs) Devices Structure based on poly[bi(5-(2-ethylhexyl)-5H-thieno[3,4-b]thiophene-alt-(4-(2-ethylhexyl)-2-fluorothieno(3,4-b)thiophene)-2-carboxylate-2,6-diyl)] (PTB7-Th):phenyl-C71-butyric acid methyl ester (PC71BM). The ITO/ZnO/TIPS-Pentacene/PTB7-Th:PC71BM/MoOx/Ag-fabricated solar cell via spin coating provides superior photovoltaic, electrical and optical characteristics when compared with the ITO/ZnO/PTB7-Th:PC71BM/MoOx/Ag solar cell. As a result, annealing temperature of TIPS-pentacene is 100°C that significantly improves the power conversion efficiency from 8.81 to 9.59% in PTB7-Th:PC71BM-based solar cells—a relative increase of 8%, which demonstrates a feasible approach to increase the efficiency of OPVs. We used synchrotron grazing-incidence wide-angle X-ray scattering, ultraviolet-visible spectroscopy, and atomic force microscopy to characterize the internal structures, transmittance, and surface roughness, respectively, of the ZnO/TIPS-Pentacene bilayer ETL films. Consequently, spin coating a slightly thin film of TIPS-Pentacene small molecule onto the ZnO layer altered the morphology of the ZnO layer and resulted in enhanced current densities, fill factors, and PCEs for the devices.

Controlling the Recombination in Ternary Organic Solar Cells—A Path Towards >14% Efficiency Nicola Gasparini1, Xin Song1, Harald Ade2 and Derya Baran1; 1KSC, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia; 2North Carolina State University, Raleigh, North Carolina, United States.

One key advantage of solution-processable organic semiconductors is the opportunity of blending different materials in order to attain novel material properties and applications. The concept of ternary blend organic solar cells makes use of exactly that idea: three (or more) organic chromophores are combined to better match the solar irradiance spectrum and thus increase the amount of light absorbed, which in turn will increase the power output of the solar cell. However, charge transport limitations of many current generation polymer blends typically require rather low active layer thicknesses (around 100 nm) for optimum performance.1 We have previously shown the design rules for non-fullerene acceptor (NF-As) and fullerene-based solar2 cells with reduced charge recombination processes leading to a high short circuit current density (Jsc) and fill factor (FF) in ternary blends. Here, we report ternary organic solar cells based on a PTB7-Th (commonly known as PCE10) donor and various non-fullerene and fullerene acceptors, by investigating the improvements in photovoltaic parameters in terms of nanomorphology and photo-physics. We utilize a dual acting third component, the small molecule donor BIT-4F-T, which enables concomitant improvement in all binary systems we have tested. By adding this third component into PTB7-Th:IEICO-4F photovoltaic devices, we are able to achieve power conversion efficiencies in excess of 14%. This ternary system clearly outperforms binary reference devices, and its conversion efficiency is among the highest values reported in the literature for ternary organic solar cells. In this study, we further clarify the underlying mechanism contributing to the efficiency of this new blend by combining charge transport measurements and microstructural investigations. We find that adding 10% BIT-4F-T increases the photon harvesting window of the photoactive layers due to its complementary absorption. Moreover, BIT-4F-T also functions as a processing-aid in the ternary systems, increasing the overall volume fraction of the highly ordered region, and thus, improves charge generation and transport. This motivated us to explore the dual effect of the third component on different non-fullerene and fullerene-based binary blends, resulting in highly efficient solar cells. Our findings reveal design rules for a third component moiety that can be used for improving all photovoltaic parameters simultaneously in ternary devices.

Gasparini et al., Energy & Environmental Science, 2017, 10, 885.

Importance of Critical Molecular Weight of Polymer Acceptor on the Mechanical and Electrical Properties of All-Polymer Solar Cells Joonhyeong Choi1, Wansun Kim2, Taek-Soo Kim2 and Bumjoon Kim1; 1Department of Chemical and Biomolecular Engineering, KAIST, Daejeon, Korea (the Republic of); 2Department of Mechanical Engineering, KAIST, Daejeon, Korea (the Republic of).

When considering application in flexible and stretchable sensors as a power source, the bulk-heterojunction (BHJ) polymer solar cell (PSC) field have attracted tremendous attention owing to their advantages like lightweight, flexibility, semi-transparency and roll-to-roll processability. In particular, the PSCs devices are inevitably exposed to repetitive bending or stretching stress, mechanical stability of devices should be guaranteed. In this regard, the all-polymer solar cells (all-PSCs) have been considered to be a successful candidates achieving high stability and efficiency. Recently, there has been successful demonstrations that the all-PSCs exhibited superior mechanical endurance compared to fullerene based PSCs (PCBM-PSCs) due to ducile characteristic of polymer acceptor and interchain entanglements, in contrast to the brittle nature of PCBM molecules. Despite these important progresses, there is a lack of an in-depth understanding on mechanical properties of all-PSCs. In this work, we investigated the molecular weight effect of n-type polymer acceptor on the mechanical and electrical properties of all-PSCs via controlling the number-average molecular weight ([M]n) varying from low to very high [M]n = 15, 20, 48, 103 and 163 kg mol⁻¹. We observed the general increasing trend of power conversion efficiency (PCE) values as a function of [M]n. In particular, the electron mobility of all-polymer blend film was found to increase by a factor of five from lowest [M]n to highest [M]n blend, while the hole mobilities are similar regardless of [M]n. These enhancement of electron mobility induced the well balanced charge transport, resulting in large increment of Jsc values. Furthermore, while the low-[M]n (15, 20 and 48 kg mol⁻¹) blend films exhibited relatively phase-separated BHJ morphology, the finely intermixed phase separation was seen in the high-[M]n (103 and 163 kg mol⁻¹) blends, indicating large interfacial area between polymer donor and polymer acceptor, which are beneficial for charge dissociation. The tensile and fracture properties followed similar trend in device performance with the higher [M]n blend films showing better mechanical robustness, but larger improvements were observed between 48 and 103 kg mol⁻¹ blend films. This better mechanical ductility of 103 and 163 kg mol⁻¹ blend films is mainly attributed to a larger fraction of amorphous regions where the interchain entanglements exist, thereby allowing to dissipate a substantial strain energy. Furthermore, we also demonstrated the contrast in mechanical compliances depending on different acceptor types (small molecule vs. polymer). Despite the very high PCE devices based on ITIC have been reported recently, the active layer including ITIC showed much inferior mechanical stability compared to that of all-PSCs due to the brittle nature of ITIC.

SYMPOSIUM ES19

Excitonic Materials and Quantum Dots for Energy Conversion
April 23 - April 25, 2019

Symposium Organizers
Joseph Luther, National Renewable Energy Laboratory
Wanli Ma, Soochow University
MingLee Tang, University of California, Riverside
Nobuhito Yanai, Kyushu University

Symposium Support
Nanoscale Advances & Chemical Science | Royal Society of Chemistry

* Invited Paper

SESSION ES19.01: Perovskite Quantum Dots
Session Chairs: Joseph Luther and Susanna Thon
Colloidal lead halide perovskite nanocrystals (APbX \(_3\) NCs, A=Cs, FA, PbI\(_2\)) have recently emerged as an alternative to conventional quantum dots, in particular, as versatile photonic sources and light-harvesting materials, due to their easily tunable photoluminescence spectra, unique exciton fine structure and facile synthesis [1-5]. A for warranting the practical utility of such semiconductor NCs in the red and infrared spectral regions, all three archetypal A-site monocationic perovskites—CH\(_3\)NH\(_2\)PbI\(_3\), CH(NH\(_2\))\(_2\)PbI\(_3\), and CsPbI\(_3\)—suffer from either chemical or thermodynamic instabilities in their bulk form. A promising approach toward the mitigation of these challenges lies in the formation of multinary compositions (mixed cation and mixed anion). In the case of multinary colloidal NCs, such as quinary Cs\(_3\)FA\(_2\)\(_x\)Pb(Br\(_y\), I\(_{3-x}\)) NCs, the outcome of the synthesis is defined by a complex interplay between the bulk thermodynamics of the solid solutions, crystal surface energies, energetics, dynamics of capping ligands, and the multiple effects of the reagents in solution. Accordingly, the rational synthesis of such NCs is a formidable challenge. We show that droplet-based microfluidics can successfully tackle this problem and synthesize Cs\(_3\)FA\(_2\)\(_x\)Pb(Br\(_y\), I\(_{3-x}\)) NCs in both a time- and cost-efficient manner. In this showcase study [6], we fine-tune the photoluminescence maxima of such multinary NCs between 700 and 800 nm, minimize their emission line widths (to below 40 nm), and maximize their photoluminescence quantum efficiencies (up to 89%) and phase/chemical stabilities. The excellent transference of reaction parameters from microfluidics to a conventional flask-based environment, thereby enabling up-scaling and further implementation in optoelectronic devices, are demonstrated as well. As an example, Cs\(_3\)FA\(_2\)\(_x\)Pb(Br\(_y\), I\(_{3-x}\)) NCs with an emission maximum at 735 nm were integrated into light-emitting diodes, exhibiting a high external quantum efficiency of 5.9% and a very narrow electroluminescence spectral bandwidth of 27 nm.

References:

5. L. Proteescu et al. ACS Nano 2017, 11, 3119-3134
6. I. Lignos et al. ACS Nano 2018, 12, 5504-5517

Exciton Fine Structure in Cesium Lead Halide Perovskite Nanocrystals

Peter C. Sercel\(^1\), John L. Lyons\(^2\), Noam Bernstein\(^3\) and Alexander L. Efros\(^2\); \(^1\)California Institute of Technology, Pasadena, California, United States; \(^2\)U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

The bright emission observed in cesium lead halide perovskite nanocrystals has recently been explained in terms of a ground bright exciton state [1], a claim which would make these materials the first known examples where the ground exciton state is not an optically forbidden dark exciton. This unprecedented claim has been the subject of intense experimental investigation which has so far failed to detect the “dark” ground exciton which is expected in electron-hole exchange models. [2,3] Here, we explore other tell-tale properties of the exciton fine structure which do not require direct measurement of the dark exciton energy in order to clarify the exciton fine structure. We review the effective mass/electron-hole exchange theory for the exciton fine structure in tetragonal and orthorhombic CsPbBr\(_3\) nanocrystals. The model requires several input parameters, including crystal field terms to parameterize the effect of the lattice distortion from the cubic to the tetragonal [4] or orthorhombic [2] perovskite phases, as well as the electron-hole exchange energy in these materials. We have employed density functional theory (DFT), together with hybrid functionals and spin orbit coupling in order to determine the crystal field parameters and the electron-hole exchange energy for the tetragonal and orthorhombic CsPbBr\(_3\) phases. With these inputs, we determine the exciton fine structure level order within the context of the exchange model. As expected, we find an optically inactive ground exciton level. However, the calculated short range exchange energy is more than an order of magnitude smaller than what would be required to explain the measured fine structure splitting within a short-range exchange model. The possible impact of long-range exchange on the fine structure splitting is discussed. Importantly, we find that even if we add the long-range exchange interaction to explain the magnitude of the splitting, the level order for the optically active excitons in tetragonal CsPbBr\(_3\) nanocrystals calculated in the exchange model is opposite to what has been observed experimentally. [2,3] An alternate explanation for the exciton fine structure splitting in CsPbBr\(_3\) nanocrystals is offered in the context of the effect of Rashba splitting on the exciton fine structure which supports the existence of the bright ground exciton in these nanocrystals.[1]

Materials that can convert absorbed photons to emitted photons with quantum efficiencies exceeding 100% are rare, but of great interest for potentially increasing the overall efficiencies of existing solar-energy conversion technologies beyond their usual thermodynamic limits. This talk will describe some of our group's recent research into understanding, controlling, and exploiting new quantum-cutting doped halide perovskite semiconductor nanocrystals and bulk materials. These unique materials combine broad absorption profiles with photoluminescence quantum yields approaching 200%, making them very attractive for solar spectral conversion in applications such as photovoltaics or luminescent solar concentration. Fundamental spectroscopic and electronic-structure properties will be emphasized as they pertain to understanding the unusual photophysics displayed by these highly luminescent materials. Specific solar applications will also be described.


efficiency of CQD solar cells has been improving quickly in recent years, with certified power conversion efficiency up to 11.3%. The use of quantum dots surface engineering effectively reduced defects and improve carriers transport. In addition, device structure engineering significantly promoted the carriers transporting and inhibited interfacial recombination. Unlike most other solar cells, both normal structure and inverted structure exhibit similar high efficiency, the efficiency of CQD solar cells with inverted structure is generally poor (below 5%). In this work, we fabricated lead sulfide CQD solar cells with inverted structure by using nickel oxide as bottom hole transporting layer. The best device shows short circuit current density of 27.6 mA/cm², open circuit voltage of 0.53 V, fill factor of 65.7% and an overall power conversion efficiency (PCE) of 9.70% under standard 1.5G solar illumination. This indicates that inverted structure, with appropriate material and interface design, could be another opportunity for more efficient CQD-based photovoltaics.

Reference:

2:00 PM *ES19.02.02
Concentration Factor Thermodynamic Limits in Luminous Solar Concentrators
Megan E. Phelan1, David R. Needell2, Halee Bauser3, Ognjen Ilic4, Colton Bukovsky5, Zachary Nett6, Brent A. Koscher7, Paul Alivisatos8, and Harry Atwater1; 1California Institute of Technology, Pasadena, California, United States; 2University of California, Berkeley, Berkeley, California, United States.

Contemporary designs for luminous solar concentrators (LSCs) employ high radiative efficiency quantum dots in order to achieve high concentration: gain ratios. However, the quantum dot LSC community suffers from a lack of consensus about geometric gain and concentration factor conventions in luminous solar concentrators (LSCs) to validate and measure device performance. In this talk, we explore inconsistencies in the definition of thermodynamic limits for LSCs in the literature, and re-evaluate their theoretical performance in a unified common framework. Using Monte-Carlo ray tracing simulations, we have modeled 6.25cm² LSCs featuring quantum dot luminescent concentrators and photovoltaics oriented in various conventional and unconventional geometries (e.g., coplanar, horizontal, edge-lined, vertical, slanted). We have performed experimental inter-comparison of concentration for LSCs in these configurations that employ highly efficient CdSe/CdS core/shell quantum dots (QDs), which absorb light in the 300-500nm wavelength range and re-emit wavelength luminescence at 635nm, a wavelength that couples to our embedded photovoltaics. The QDs are dispersed throughout a 3.2 mm thick poly(laurylmethacrylate) (PLMA) waveguide layer and the photovoltaic is oriented within the waveguide, according to each target geometry. We standardized each device configuration to conform to a geometric gain of 120. Through our simulations, we have explored the radiative limit for each geometry. These simulations reveal significant discrepancies in measured power output and power conversion efficiency between the different cell geometries tested, and are compared to photovoltaics measurements of fabricated LSC prototypes for each cell geometry. During this talk, we will discuss how performance metrics of LSCs go beyond concentration factors and towards efficiency. We will further propose a new framework for LSC device performance, which aligns with theoretical thermodynamic limits and can be measured experimentally. Our analysis has the potential to standardize performance measurements in the LSC community, independent of device geometry, luminescent, photovoltaic material, or waveguide form factor.

2:15 PM *ES19.02.03
PbS QD/ZnO Nanowire Solar Cells for Series-Connected Triple-Junction Solar Cells with Approximately 30% Efficiency
Takawa Kudo; Hailbin Wang, Shiochiro Nakao, Naoya Miyashita, Yoshihata Okada, Tetsuya Hasegawa, Jota Nakazaki and Hiroshi Segawa; The University of Tokyo, Tokyo, Japan.

In developing low-cost and ultra-high efficiency solar cells, the utilization of the photon energy in a wide range of the solar spectrum is crucial. However, the theoretical maximum of the power conversion efficiency of single-junction solar cells under one-sun illumination remains 31% at best. To surpass the single-junction limit, several concepts have been proposed, including multiple exciton generation, hot-carrier, and intermediate band. Among these concepts, the multi-junction concept has only been proven to overcome the single-junction limit, and multi-junction solar cells are commercially available. However, multi-junction solar cells that can surpass the limit are expensive to fabricate, which hampers the large-scale implementation of solar cells. Thus, development of multi-junction solar cells with low-cost technologies such as solution-based fabrication processes would help to expand their implementation.

Although there have been several reports on multi-junction solar cells including solution-based subcells such as perovskite solar cells, most of the solution-processed solar cells were used as top subcells [3, 4], but little has been reported for solution-processed bottom cells. The highest power conversion efficiency reported so far on solution-processed multi-junction solar cells (Perovskite top subcell/Si bottom subcell) stands at 25.2% at best. We then focused on infrared PbS CQDs and ZnO nanowires (NWs) approximately 1µm long, and constructed heterojunction hybrid structures. The PbS QD/ZnO NW hybrid structures forming a bulk-heterojunction allow almost all the photo-generated carriers to reach the PbS QD/ZnO NW interface even when the active layer is thicker than the carrier diffusion lengths. Our recent study revealed that PbS QD/ZnO NW solar cells could be used to convert a wide range of solar energy to electricity [1, 2].

In the presentation, we report high efficiency infrared PbS QD/ZnO NW solar cells that produce sufficiently large photocurrent in the infrared region, and the results of a proof-of-concept study for multi-junction solar cells.

We constructed infrared PbS QD/ZnO NW solar cells, with the aim of developing solution-processed multi-junction solar cells. Morphology of 1-µm-long ZnO nanowires was optimized, which allowed us to construct otherwise difficult, spatially separated carrier pathways and thick PbS QD layers for high infrared light harvesting. The optical management together with highly infrared-transparent conductive oxide (Ta-doped SnO2; TTO) electrodes were successfully used to enhance the spectral sensitivity in the infrared region. The external quantum efficiency of the solar cell reached 47% at the wavelength corresponding to the first exciton peak (1560 nm): this is the highest value ever reported on the solution-processed solar cells.

We fabricated series-connected triple-junction solar cells by combining the PbS QD/ZnO NW solar cell (as a bottom subcell) with III-V JZ solar cells (InGaP top subcell/GaAs middle subcell). The series-connected triple-junction solar cell achieved approximately 30% under one-sun illumination, verifying that the PbS QD/ZnO NW solar cells have a great potential for solution-processed bottom subcells.


2:30 PM *ES19.02.04
Transport in Quantum Dot Solids
Vanessa Wood; Dept. of Information Technology and Electrical Engineering, ETH Zürich, Zurich, Germany.

This talk will describe why. I will begin by describing the type of structural dynamics that occurs in quantum dot solids and the methods that we can use to measure structural dynamics, such as inelastic neutron scattering and inelastic x-ray scattering, or simulate it, such as ab initio molecular dynamics. Then I will describe the theory of how electrons and vibrations interact, and the challenges we face in calculating non-radiative electronic transitions rates. Finally, I will explain why we should care about structure dynamics, specifically the impact the type of dynamics has on electronic properties such as mobility and Shockley Read Hall non-radiative recombination. In my talk, I will rely on the example of PSS NCs and present a predictive model for electronic and thermal transport. Furthermore, I will describe how changing the structural dynamics (e.g., by changing the surface of NCs) can be used to systematically change the transport by reducing both the thermal displacement of surface atoms and the spatial overlap of the charge carriers with these large atomic vibrations.

3:00 PM BREAK

3:30 PM *ES19.02.05
Pre-Exchanged Quantum Dot Ink Based Solar Cells
Sung-Yeon Jang; Department of Chemistry, Kookmin University, Seoul, Korea (the Republic of).

Colloidal quantum dot (CQD) based solar cells have emerged as one of the most promising low cost power generators owing to their easy bandgap tunability and solution processability. Recently, the power conversion efficiency (PCE) of CQD solar cells has been expanded to >12% by the development of high-quality CQD materials and device
architectures. However, the fabrication of CQD solar cells often includes tedious multiple layer-by-layer deposition (LbL) by solid-state ligand exchange (SSE), which has been a major obstacle to high-throughput processing. Development of pre-formed CQDs which do not require LbL/SSE procedure will be beneficial for the view point of device fabrication. In this talk, the development of pre-exchanged n-type and p-type CQD inks, and the fabrication of CQD solar cell devices by direct coating method will be presented. Using these CQD inks, the PCE of –11% was achievable. Moreover, the application of doctor-blade coating method was also feasible, which suggests its potential use in other industrially-friendly processes.

4:00 PM ES19.02.06
Ligand Passivation Strategies for CsPbX Nanocrystals Ashley Marshall; Olivia J. Ashton, Bernard Wenger and Henry Snaith; Physics, University of Oxford, Oxford, United Kingdom.

Despite the improvements seen in efficiency of GaAs cells over the years, there remains room for improvement for it to approach the theoretical single junction limit posited by Shockley and Queisser decades ago. One of the most pursued options is the growth of quantum wells within the structure of GaAs to enhance its photon absorption below its bandgap. Multiple Quantum Wells (MQW) have been an ongoing topic of research and discussion for the scientific community with structures like InGaAs/GaAs and InGaP/GaAs quantum wells producing promising results that could potentially improve overall energy conversion. Here, we used WEI2NK, a commercial density functional theory package, to study the ternary compound GaInAs and determine its electronic properties. Using these results combined with experimental confirmation we extend these properties to simulate its application to form a MQW GaAs/GaInAs solar cell. GaInAs is a tunable ternary compound, with its bandgap being strongly dependent on the concentration of In present. Concentrations of In as low as 7% can reduce the bandgap of GaInAs to roughly 1.30 eV from GaAs’s 1.45 eV at room temperature with as little as a 1.7% increase in lattice constant. The change in bandgap, accompanied by the relatively small change in lattice constant makes GaInAs a strong candidate for a MQW cell with little to no strain balancing required within the structure to minimize unwanted defects that impede charge collection within the device. Our GaAs photodiode with TiGaAs MQWs shows an expanded absorption band and improved conversion efficiency over the standard GaAs photovoltaic cell with dilute concentrations of In incorporated into the compound.

4:15 PM ES19.02.07
RGB QLED Device Prepared by Inkjet Printing with Mixed Solvent and Printing Route Tai Yu-Chieh, Shih-Jung Ho, Kuo-Yang Lia and Hsueh-shih Chen; Material Science and Engineering, National Tsing Hua University, Hsinchu City, Taiwan.

Quantum dot (QD) technology has received a lot of attention for the advantages of high quantum yield (QY), narrow full-width at half-maximum (FWHM) and tunable wavelength. Recently, photoluminescence-based QD LCD display equipped with QD film as a light converter has been commercialized. In the near future, electroluminescence QLED is expected to be a next generation display competing with other potential flexible displays. With a similar device structure of OLED, QLED display based on inorganic quantum dots would possess better stability, more color purity and wider color gamut than other displays. Moreover, QD layers in the device are compatible with solution processing, which makes QLED display can be easily scaled up to a large area, mass productive and cost effective. In this research, a solution-processed QLED device with a structure of ITO/PEDOT:PSS/PVK/QD/ZnO/Al was prepared with spin-coating and inkjet-printing. A QD ink with mixed solvent has been developed to reduce coffee-ring effect and enabling light absorptions at higher wavelength regions. QD size manipulation via the microwave technique was further confirmed via transmission electron microscopy (TEM). The properties of CdSe QDs makes them suitable candidates for tunable band gap light harvesting, and plans are in place to incorporate them in P3HT:PCBM heterojunction solar cells as a means of increasing their solar energy power conversion efficiency (PCE).

Funder Acknowledgement(s): This work is supported by the NSF-CREST Grant number HRD 1547771 and NSF-CREST Grant number HRD 1036494.

ES19.03.01
Size-Tunable Synthesis of Cadmium Selenide Quantum Dots to Increase Solar Cell Efficiency Jacob Strimaitis, Taliya Gunawansa, Sangram K. Pradhan and Messaoud Bahoura; Norfolk State University, Norfolk, Virginia, United States.

Colloidal quantum dots (QDs) present a promising solution to the problem of attaining cheap, size-tunable light harvesters for third generation solar cells. Cadmium Selenide (CdSe) QDs were synthesized using a one-pot microwave irradiation technique to meet this need. Synthesized quantum dots showed excellent luminescent behavior under UV lamp, which was further confirmed by other spectroscopic techniques. Photoluminescence (PL) and ultraviolet-visible spectroscopy (UV-VIS) spectra revealed that changing the time and temperature of the microwave during synthesis changed the size of the QDs from a few nanometers to tens of nanometers, causing their fluorescence intensity to red shift and enabling light absorptions at higher wavelength regions. QD size manipulation via the microwave technique was further confirmed via transmission electron microscopy (TEM). The properties of CdSe QDs makes them suitable candidates for tunable band gap light harvesting, and plans are in place to incorporate them in P3HT:PCBM heterojunction solar cells as a means of increasing their solar energy power conversion efficiency (PCE).

Funder Acknowledgement(s): This work is supported by the NSF-CREST Grant number HRD 1547771 and NSF-CREST Grant number HRD 1036494.

ES19.03.03
Efficient Production of Ultraviolet Light from Kinetically Controlled Synthesis of CdS Nanocrystals Paulina Janies; University of California, Riverside, Riverside, California, United States.

Es19.02.06 GaTiAs Quantum Well Solar Cells for Sub-Band Gap Absorption Ahmed Zayan and Thomas E. Vandervelde; Renewable Energy and Applied Photonics Laboratory, Electrical and Computer Engineering Department, Tufts University, Medford, Massachusetts, United States.
Few methods currently exist to produce UV light from lower energy photons. UV light is useful in photocatalysis and many applications of light in the biological disciplines. The highest photon up-conversion quantum yield for the production of UV light from visible light is 5.2% ± 0.5 using CdS nanocrystals (NC) light absorbers. Here the goal is to increase the energy transfer efficiency with higher quality CdS NCs. Specifically, we investigate a variety of sulfur containing precursors to kinetically controlled nucleation to yield different sizes of CdS NCs with peak absorbances ranging from 398nm to 453nm. The CdS NCs made were characterized using optical absorption and photoluminescence spectroscopy. The goal is to eliminate the current need for the ZnS shell with CdS NCs that have minimal surface trap states. The next step will be to bind ligands to the NC and optimize upconversion parameters. We will report the photon upconversion QYs with 2-naphthoic acid transmitter ligands that enhance triplet energy transfer from CdS NCs to 2,5-diphenyloxazole emitter.

ES19.03.04
Zinc Thiolate Determines the Identity of ZnS Shells on Cu-Deficient Cu-In-S QDs

Frie Hansen, Sophie Bertram, Jason Yoo and Mounqi Bawendi; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Copper Indium Sulfide (CIS) colloidal quantum dots (QDs) are promising candidates for commercially-viable QD-based optical applications, for example as colloidal photocatalysts or in luminescent solar concentrators (LSCs). CIS QDs with good photoluminescence quantum yields (PLQYs) and tunable emission wavelength via size and composition control have been previously reported. However, developing an understanding and control over the growth of electronically-passivating inorganic shells would enable further improvements of the photophysical properties of CIS QDs. To improve the optical properties of CIS QDs, we focus on the growth of inorganic shells via the popular metal-carboxylate/alkane thiol decomposition reaction. We (1) study the role of Zn-carboxylate and Zn-thiolate on the formation of ZnS shells on Cu-Deficient CIS (CDCIS) QDs, (2) leverage this knowledge to yield >90% PLQY CDCIS/ZnS core/shell QDs, (3) demonstrate control over interfacial alloying, and (4) propose a mechanism for ZnS shells grown from zinc-carboxylate/alkane thiol decomposition.

ES19.03.05
Novel Dendritic Large Molecules Exhibiting Thermally Activated Delayed Fluorescence for Simple-Processed Organic Light Emitting Diodes

Hyung J. Kim, Seo Yeon Park, Mallesh Godumula, Su Hong Park, Choe Hoon Jeong, Jiwon Yoon, Chae Yeong Kim, Min Ju Cho and Dong Hoon Choi; Korea University, Seoul, Korea (the Republic of).

Recently, research on an organic light emitting diode (OLED) based on thermally activated delayed fluorescence (TADF) having a high internal quantum efficiency is being actively conducted. In particular, it is recognized that OLED by solution process can be applied to large display devices and flexible display manufacturing because manufacturing process is simple and large area device can be manufactured. In this presentation, we have demonstrated a series of new dendritic TADF emitters applicable in simple structured or all soluble OLEDs. All these new materials exhibit excellent solubility in common organic solvents and apparent TADF characteristics. The TADF emitters used in simple structured OLEDs without any HIL or HTL realized excellent performance with the high EQE. Besides, another series of TADF emitters displaying aggregation induced emission employed in all soluble OLEDs achieved EQE as high as 11%. Therefore, we strongly believe that these results will definitely open the doors to develop “simple structured OLEDs” instead of conventional OLEDs consisting complicated multi-layered device structure and difficult fabrication procedures.

ES19.03.06
Lanthanide Decorated Semiconductor Quantum Dots for Use as Broadly Absorbing Downshifters

Joseph Swaebuck, Stefan Fischer, Noah Bronstein and Paul Alivisatos; 1,2 Department of Chemistry, University of California, Berkeley, Berkeley, California, United States; 3Materiors Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Kavli Energy NanoScience Institute, Berkeley, California, United States.

Luminophores with sharp emissions coupled to broad absorption have many applications including solar energy harvesting. Lanthanide ions have very sharp, typically ~10 meV FWHM, emissions that are largely insensitive to temperature or surrounding environment. However, lanthanides do not absorb well outside of these transitions, so their ability to act as luminophores is limited. Doping semiconductors with lanthanides has been pursued in thin films, but these systems typically only show luminescence at cryogenic temperatures. As such, we seek to place lanthanides onto quantum dots to combine the broad absorption of nanomaterials with the narrow emission of the lanthanides. We use lanthanide trifluoroacetates and standard hot injection processes to grow an optically active Yb doped shell around InP quantum dots. The particles are then characterized via a variety of optical and structural methods. The structural methods, which include high resolution electron microscopy, elemental mapping, and extended x-ray absorption fine structure measurements, show that the nanoparticles take on a core/shell structure. Optically, we are able to see that there is a near infra-red emission upon excitation with UV/visible light. The emission is traced back to the quantum dot absorption via a photoluminescence excitation measurement, while the lifetimes of the near infra-red emission show that the Yb ions are somewhat passivated from the surface of the nanoparticle. This work shows the synthesis, optical, and structural characterization of Yb decorated InP quantum dots. These materials could be used as stable and sharp luminescence centres in the near infra-red and beyond.

ES19.03.07
Critical Casimir Forces Drive Quantum Dot Epitaxy

Emanuele Marino, Bas B. Kluft, Thomas E. Kodger and Peter Schall; 1Institute of Physics, University of Amsterdam, Amsterdam, Netherlands; 2Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Physical Chemistry and Soft Matter, Wageningen University & Research, Wageningen, Netherlands.

Epitaxy is at the basis of many fabrication protocols in the semiconductor industry, allowing the development of complex architectures for optoelectronic devices. Epitaxial growth critically depends on the interaction between adsorbing particles, and between the particles and the substrate. While this process has been demonstrated for both atoms and microparticles,1,2 the intermediate case of nanocrystals has remained elusive due to our limited understanding of interparticle interactions at the nanoscale.3 Here, we demonstrate the epitaxial growth of semiconductor nanocrystals, quantum dots (QDs), on a flat, unfunctionalized and unpatterned silicon substrate via critical Casimir forces. By tuning the interplay of attractive critical Casimir and repulsive electrostatic interactions, we show that the epitaxial process can be biased towards either 2D layer or 3D island growth, consisting of crystalline or amorphous superstructures. These results demonstrate the potential of the critical Casimir interaction to direct the growth of future artificial solids based on QDs as fundamental building blocks.


SESSION ES19.04: Singlet Fission and Downconversion
Session Chairs: Sean Roberts and Nobuhiro Yanai
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 132 A
In recent years, quantum dots (QDs) have gained interest as narrowband emitters for displays, but have traditionally suffered from reliability issues, high manufacturing cost, and toxicity concerns, which prevent them from being incorporated into products beyond displays. At UbiQD, we envision making QDs ubiquitous across many industries with a new kind of QD that is intrinsically more stable, lower-cost, and avoids toxic compounds. We are first focusing on bringing to market QD-tinted films and glass for spectrum-optimized greenhouses. This talk will highlight the recent developments including data from several commercial greenhouse pilot projects, and an overview of the first-ever QD greenhouse product.

8:30 AM *ES19.04.02
Up- and Down-Converting Photons in Molecular Singlet Fission Materials Dirk M. Guldi; University of Erlangen-Nuremberg, Erlangen, Germany.

The Shockley-Queisser limit places an upper bound on solar conversion efficiency for a single p-n junction solar cell at slightly more than 30%. To surpass this limit, multi-exciton generation is being explored in inorganic semiconductors, while singlet fission (SF) is being investigated in arrays of conjugated organic molecules. In an optimal SF process, the lowest singlet excited state of one molecule ($S_1$) that is positioned next to another molecule in its ground state ($S_0$) is down-converted into two triplet excited states ($T_1$) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state ($S(T_1)$), which then evolves into two separated triplet states ($T_1 + T_1$). As such, the energetic requirement for SF is $E(S_1)$ larger than 2 $E(T_1)$.

We have set our focus in recent years on intramolecular SF in molecular materials and their studies in solution rather than on intermolecular SF investigations in crystalline films. Implicit in intramolecular SF is a resonant, direct excitation of the SF material. In pentacene dimers linked by a myriad of molecular spacers, SF takes place with quantum yields of up to 200%. In addition, all key intermediates in the SF process, including the formation and decay of a quintet state that precedes formation of the pentacene triplet excitons, have been identified. This approach is, however, limited to the part of the solar spectrum, where, for example, the pentacene dimers feature a significant absorption cross-section. To employ the remaining part of the solar spectrum necessitates non-resonant, indirect excitation of the SF materials via either up- or down-conversion. For example, the up-conversion approach is realized with singlet excited states in pentacene dimers, which are accessed by two-photon absorptions (TPA). TPA is then followed in the second step of the sequence by an intramolecular SF – similar to what is seen upon resonant, direct excitation. Quite different is the down-conversion approach, which is based on an intramolecular Förster resonance energy transfer (FRET) and thereby the (photo)activation of the SF material. FRET requires the use of a complementary absorbing chromophore and enables funneling its excited state energy unidirectionally to the SF performing pentacene dimer. Again, SF completes the reaction sequence.

9:00 AM ES19.04.03
Counting Triplets on Single Polymer Chains for Solar Cells Benjamin D. Datko1,2, Martin Heeney1, Kevin J. Noonan3 and John Grey1; 1University of New Mexico, Albuquerque, New Mexico, United States; 2Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 3Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, United Kingdom.

Current optimization of organic solar cells has hit a wall with optimal power conversion efficiencies stagnating at 12.5 % with only small incremental changes in the past five years. Conjugated polymers are still advantageous to improve organic solar cells, but it is difficult to correlate the structure-activity of these materials due to their intrinsic heterogeneity. To effectively iterate over new molecular design strategies targeting multiple exciton generation (MEG) through heavy atom substitution and singlet fission, new insights are needed. Here we use single molecule photomodulation spectroscopy to resolve multiple triplet populations at the single chain level. This technique ascertains the pulse-induced kinetics of triplet formation through synchronous averaging of the fluorescence emission with a high repetition rate of square pulse excitations. Thus, allowing to resolve singlet-triplet dynamics intrinsic to the conjugated polymer. In parallel, we have utilized the solutions to the probabilistic master equation describing the time-dependent kinetics of triplet formation. Using measured rates from our experiments we can now count the most likely number of triplets on the conjugated polymer. Measuring poly-3-hexylthiophene (P3HT), poly-3-hexyl-selenophene (P3HS), and combinations of S-Se heterocycles containing polymers we can systematically map the kinetics of triplet formation to the structure activity for these materials.

9:15 AM ES19.04.04
Conformational Preference for Triplet Production in Multichromophoric Molecules via Single Molecule Spectroscopy David J. Walwark, Benjamin D. Datko and John Grey; University of New Mexico, Albuquerque, New Mexico, United States.

Multichromophoric molecules have great potential in optoelectronic applications but their electronic properties are extremely sensitive to conformation, making molecular design difficult. We employ modulated polarized light to interrogate single molecules of tetrakis(perylene-diimide) spiro-bifluorene, simultaneously correlating ordering and photophysics, with a focus on triplet dynamics with excimeric parentage. Widefield fluorescence microscopy excels at building reliable distributions of photophysical states via quantified fluorescence response to modulated linearly polarized excitation. Allowing the analyte to react with oxygen during the experiment lets us implicate certain levels of ordering with increased production of triplet excited states. Further analysis with confocal microscopy in oxygen-free conditions links emission lifetimes and microsecond emission dynamics explicitly to single-chromophore and excimer excited states via dichroic detection. Using linear polarization modulation across all experiments combines the robust statistical distributions and proven oxygen reactivity of the widefield results with the fast timescale sensitivity of the confocal data to yield a comprehensive photophysical profile of multichromophoric arrays in a polymer environment.

9:30 AM *ES19.04.05
Polariton Assisted Photophysics—Remote-Energy Transfer, Singlet-Fission and Triplet Harvesting Joel Yuen-Zhou; University of California, San Diego, La Jolla, California, United States.

When an ensemble of molecules interacts with the optical modes of a microcavity or an electromagnetic nanostructure, the collective excitations of the strongly coupled light-matter (polariton) system are no longer purely molecular nor electromagnetic, but hybrid superpositions of the two. In this talk, I will discuss our recently developed theoretical models that explain the mechanisms whereby polaritons can enhance excitonic processes such as singlet-fission and harvesting of triplets in organic materials.

10:00 AM BREAK

10:30 AM *ES19.04.06

Singlet fission in organic semiconductors provides an efficient means to achieve exciton multiplication. To realise useful applications for efficiency enhancement in photovoltaic devices requires that the energy of each of the triplet excitons is efficiently harvested. I will describe an all-optical approach where triplet excitons from fission are transferred to inorganic semiconductor nanoparticles which can then emit at energies close to the photovoltaic bandgap. The challenge here is to achieve high efficiencies for nanoparticle luminescence whilst still allowing triplets to tunnel into the particles. I will describe measurements where fission takes place in solution and the triplets are efficiently transferred to nanoparticles. The key to achieving this is the use of acene ligands attached to the particles, providing adequate passivation of the particles whilst facilitating the transfer of triplets into the particles.

I will also describe measurements using electron spin resonance and luminescence at high magnetic fields to probe the interactions between triplets generated by fission in acene
films. These measurements demonstrate the presence of bound triplet pairs with overall singlet, triplet and quintet characters, and allow their binding energies to be determined. I will present recent results using transient electron spin resonance techniques and magneto-photoluminescence at very low temperatures to study the mechanisms by which quintet pair states are formed from pair states with initial singlet character.

11:00 AM ES19.04.07
Singlet Fission in Designed Architectures for Triplet Exciton Harvesting  Justin Johnson1, Nadia Korovina1, Natalie Pace1, 2, Melissa Gish1, Obadiah Reid1, 2 and Garry Rumbles1, 2; National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2University of Colorado Boulder, Boulder, Colorado, United States.

Approaches to utilizing triplet excitons born from singlet fission require consideration of schemes for triplet state lifetime elongation and either exciton dissociation or energy transfer. To isolate triplets after singlet fission, molecular design principles can be used to provide pathways for exciton migration and localization. Subsequently, an interface with a charge or energy acceptor can be introduced. This interface and the associated dynamics have nanoscale components and are often complex structurally and chemically. I will describe our efforts to characterize charge and energy transfer at interfaces involving singlet fission molecules and designed molecular charge acceptors, quantum dots, and oxides. In some cases molecular assembly at the interface naturally alters the intermolecular coupling and thus the intrinsic singlet fission dynamics, which leads to a kinetic competition between various pathways that is challenging to elucidate. Covalently bound chromophores (i.e. dimers and oligomers) can then be attractive alternatives due to their well-defined interchromophore geometries. We use a combination of synthesis, electrochemistry, and various forms of transient spectroscopy to monitor the relationship that molecular structure and electronic state energies have on the processes of singlet fission, exciton migration, energy transfer, and exciton dissociation.

11:15 AM ES19.04.08
Two Temperature Regimes of Triplet Transfer in the Dissociation of the Correlated Triplet Pair in Singlet Fission  Jin Lee1, YunHui L. Lin2, Hwon Kim3, Barry P. Rand4, 5 and Gregory D. Scholes1; 1Chemistry, Princeton University, Princeton, New Jersey, United States; 2Electrical Engineering, Princeton University, Princeton, New Jersey, United States; 3Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey, United States.

The ability to undergo spin-allowed exciton multiplication makes singlet fission materials promising for photovoltaic applications. The majority of studies to date have emphasized understanding the first step of singlet fission, where a correlated triplet pair is produced. Here we examine the separation of correlated triplets, \( \langle T^+ T^- \rangle \), in polyacrylamide pentacene films via temperature dependent transient absorption spectroscopy. Single wavelength analysis reveals a profound delay in \( \langle T^+ T^- \rangle \) dynamics. Moreover, the dynamics of \( \langle T^+ T^- \rangle \) exhibit temperature dependence while other features shown discernable temperature dependence. Previous literature have suggested that correlated triplet separation is mediated by a thermally activated hopping process. Surprisingly, we find that the time constants governing triplet pair separation display two distinct temperature-dependent regimes of triplet transport. The high temperature regime follows a thermally activated hopping mechanism. The experimentally derived reorganization energy and electronic coupling is verified by density matrix renormalization group quantum chemical calculations. In addition, we evaluated the low temperature regime and show that the trend can be modelled by a Miller-Abrahams-type model that incorporates the effects of energetic disorder. We conclude that the correlated triplet pair separation is mediated by thermally activated hopping or a disorder driven Miller-Abrahams-type mechanism at high and low temperature, respectively. We observe that the time constants governing triplet pair separation is mediated by thermally activated hopping or a disorder driven Miller-Abrahams-type mechanism. The high and low temperature regimes are – 226 K. We find the time constant for triplet-triplet energy transfer to be 1.6 ps at ambient temperature and 21 ps at 77K.

11:30 AM •ES19.04.09
The Potential of Singlet Fission for More Efficient Solar Cells  Bruno Ehler; Center for Nanophotonics, Institute AMOLF, Amsterdam, Netherlands.

Singlet fission, the conversion from one high-energy singlet exciton into two lower-energy triplet excitons in organic semiconductors can be used to overcome the Shockley-Queisser efficiency limit for single-junction solar cells. However, increasing the photocurrent by singlet fission requires efficient charge generation from triplet excitons. While such charge generation has been shown in purely organic solar cells, and in quantum dot/organic hybrids, it has never been shown in combination with the most important solar cell material, silicon.

Here we will first calculate the efficiency potential of such singlet fission solar cells given realistic device parameters. We will show how the efficiency depends on the quantum yield of all processes, the optical properties, and the energetics involved. This model reveals that direct charge transfer from the triplet exciton allows for the highest efficiency gain compared to more indirect paths, and, surprisingly, that the highest efficiency can be achieved with a relatively low (singlet) bandgap of around 1.9 eV.

With optimistic, but realistic device parameters, the efficiency of the record-efficiency silicon solar cell could increase from 27% to 38%, even more than optimistic models predict for tandem solar cells. We will also show that singlet fission cells behave differently than tandem cells under real-life operation conditions, and have a different dependence on the silicon base-cell efficiency. Finally, we will present experimental evidence for charge transfer on aromatically passivated silicon surface using a spatially-resolved quenching experiment.
Many inorganic semiconductors of interest for solar energy conversion applications have indirect band gaps, which means that access to the lowest energy excited state via photon absorption requires coupling to a lattice phonon. The most famous example of an indirect semiconductor used in solar energy conversion is, of course, silicon, but many metal oxide semiconductors that have recently emerged as promising photoelectrodes for solar fuels generation, such as BiVO₄ and CuFeO₂, also have indirect band gaps. This talk presents recent data that identify spectral signatures of indirect transitions in transient absorption spectra of solution-processed nanostructured thin films of transition metal oxide semiconductors. Comparison of transient absorption spectra to thermal difference spectra generated by taking the difference between a steady-state absorption spectrum collected at elevated temperature and one collected at room temperature enables distinction of spectral features associated with thermal energy (i.e., phonons) in the semiconductor lattice from features associated with purely electronic transitions of photoexcited carriers. These distinctions not only enable accurate assignment of transient absorption spectra of metal oxide thin films, which is critical to their meaningful interpretation, but they also provide a means to probe directly the generation and evolution of thermal lattice energy in these films. Further characterization of these thermal processes will provide important insights into the function of metal oxide thin film semiconductors in devices for solar energy conversion.

2:30 PM BREAK

3:30 PM *ES19.06.01
Designing Organic—Inorganic Junc tions for Photon Conversion
Michael S. Azzaro, Jon A. Bender, Emily Raulerson, Inki Lee and Sean T. Roberts; Chemistry, The University of Texas at Austin, Austin, Texas, United States.

The negligible spin-orbit coupling in many organic molecules creates opportunities to alter the energy of excited electrons by manipulating their spin. In particular, molecules with a large exchange splitting have garnered interest due to their potential to undergo singlet fission (SF), a process where a molecule in a high-energy spin-singlet state shares its energy with a neighbor, placing both in a low-energy spin-triplet state. When incorporated into photovoltaic and photocatalytic systems, SF can offset losses from carrier thermalization, which account for ~50% of the energy lost by these technologies. Likewise, compounds that undergo SF’s inverse, triplet fusion (TF), can be paired with infrared absorbers to create structures that upconvert infrared into visible light. However, designing functional applications based on either of these processes requires organic/inorganic junctions that readily transfer energy from one material to the other. In this presentation, we will describe our group’s recent efforts to produce organic/inorganic junctions that transmit excitons in a particular spin state. Specifically, we will describe work examining peryleneimide (PDI) films grown on Si(111) surfaces. Photoexcitation of the PDI layer produces a spin-singlet exciton that undergoes SF over a few hundred picoseconds to yield a triplet exciton pair. Transient reflectivity measurements indicate these triplets exhibit a reduced lifetime in PDI:Si bilayers relative to PDI films grown on quartz, suggesting triplet energy transfer from PDI to Si. We will also describe work on quantum dot superlattices wherein the quantum dot surface ligands have been replaced with exciton delocalizing ligands, molecules with valence orbitals that strongly hybridize with quantum dot band edge states. We have recently show ligands of this type can significantly speed exciton transport in quantum dot solids, leading to dot-to-dot energy hopping rates as short as 200 fs.

Work using exciton delocalizing ligands to produce quantum dot structures that effectively deliver energy to triplet excitons accepting molecules for photon upconversion will be described.

4:00 PM *ES19.06.02
Photon Upconversion in Molecular Assemblies and Hybrid Materials
Nobuhiro Yanai¹, ²; ¹Department of Chemistry and Biochemistry, Kyushu University, Fukuoka, Japan; ²JST-PRESTO, Kawaguchi, Japan.

We show exciting research opportunities when the concept of molecular self-assembly meets photon upconversion (UC) based on triplet-triplet annihilation (TTA). In dense dyne assemblies, triplet excitons can efficiently migrate and annihilate. Highly efficient photon upconversion has been realized in a wide range of chromophore assemblies, such as non-solvent liquids, ionic liquids, amorphous solids, gels, supramolecular assemblies, liquid crystals, and crystals. The control over their assembly structures allows for unexpected air-stability and efficient upconversion at weak excitation intensity.

In addition, we would like to introduce our recent progress in developing new UC mechanisms. NIR-to-vis UC is particularly important for various applications, however, it remains challenging mainly due to the energy loss during the S₁-to-T₁ intersystem crossing (ISC) of sensitizers. We circumvent this energy loss by employing a sensitizer with direct S₂ absorption in the NIR region. Sensitizer-doped emitter nanoparticles are dispersed into an oxygen-barrier polymer. The obtained composite film shows a stable NIR-to-vis UC even in air, expanding the scope of molecular sensitizers for NIR-to-vis UC.

We have also unveiled the potential of three-dimensional (3D) metal-halide perovskites to sensitize organic triplets. Nanocrystals of surface-modified inorganic cesium lead halide perovskite CsPbX₃ (X = Br/I) are found to work as efficient triplet sensitizers for TTA-UC at low excitation intensity.

References

4:15 PM *ES19.06.03
Photon Upconversion—Novel Annihilators for Photoedox Catalysis
Andrew Pun¹, Luis Campos¹ and Dan Congreve²; ¹Columbia University, New York, New York, United States; ²Rowland Institute at Harvard University, Cambridge, Massachusetts, United States.

Photon upconversion is the process by which low energy photons are converted into one higher energy photon. This process has seen wide advancements in recent years owing to its broad scope of potential applications. However, the number of materials that can be used as upconversion annihilators are quite limited. Here I will discuss our groups’ efforts towards expanding the library of annihilators for upconversion. This includes exploring new families of chromophores, as well as synthetic modifications to existing materials for more efficient upconversion. Finally, I will detail a new application of upconversion: performing photoedox catalysis with infrared radiation.

4:30 PM *ES19.06.04
Progress Using Hybrid Nanomaterials for Excitonic Photon Conversion
Mark W. Wilson; Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

The ability to efficiently convert low-intensity light between the visible and infrared would be an enabling technology—particularly for applications such as 3rd-generation photovoltaics, biological imaging, and cost-effective sensitized silicon focal plane array detectors with response in the short-wave infrared (SWIR; λ:1–3µm). Accordingly, we are advancing recent approaches that combine two excitonic materials—organic semiconductors and colloidal nanocrystals—to achieve broadband, non-coherent photon up-
The dynamics of electronic degrees of freedom is propagated by a Redfield equation of motion for the reduced density matrix. The influence of momentum dispersion on hot-electron relaxation rates and nonradiative lifetimes for SiNWs with <100> and <111> crystallographic directions. Photoexcited dynamic processes in semiconductor nanowires are influenced by continuous sampling of momentum in growth direction. Here, motivated by our previous studies, we show that the electron relaxation time in <100> SiNW is longer than in <111> SiNW. Our study also indicates that the electron relaxation time in <100> SiNW is longer than in <111> SiNW.

Multifunctional phosphor nanoparticles based on lanthanide ions have gained significant interest due to their potential applications in various multifunctional devices for solid-state lighting, optoelectronics, and scintillation. Currently, it is a big challenge to synthesize nanophosphors with high emission intensity, radioluminescence (RL) efficiency and excited state lifetime comparable to traditional phosphors. In this work, La2H2O3:Sm3+ (LHOS) nanoparticle (NPs) prepared by a molten salt synthesis method at relatively low temperature have characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The LHOS NPs show highly efficient, orange-red emitting properties as UV-based phosphor. X-ray scintillator and luminescence thermal decay kinetics study is carried out for both photoluminescence (PL) and RL. The emission characteristics show different behaviors under UV and X-ray excitations in terms of controlling magnetic dipole transitions. When LHOS NPs are exposed to energetic X-ray beam, Sm3+ ions situated at symmetric environment get excited along with those located at asymmetric environment, which results in high asymmetry ratio of Sm3+ under RL compared to PL. The PL and RL mechanisms are proposed based on Van Uitert equation. The important parameters such as thermal quenching activation energy and thermal sensitivity are also evaluated to evaluate the performance of the LHOS NPs as a thermal sensor. Our results indicate that these samarium activated Ln2H2O3:NP can serve as UV, X-ray and thermographic phosphor.

The synthesis of two-dimensional GaN offers new opportunities for this important commercial semiconductor in optoelectronic devices because the extreme quantum confinement enables additional control of its optical properties. Using first-principles calculations based on many-body Green’s function theory, we demonstrate that in monolayer GaN, a large band gap of 5.387 eV is governed by enhanced electron–electron correlations. Strong electron-hole interactions due to weak screening lead to strongly bound excitons with a large binding energy of 1.272 eV. These tightly bound excitons result in a strong absorption peak in the middle ultraviolet region. The dynamical screening between electron–hole pairs is totally different from bare Coulomb interaction. Long quasiparticle (quasielectron, quasihole, and exciton) lifetimes are observed as a result of the many-body interactions. Because of the large binding energies, long exciton lifetimes, and large quantum degeneracy, an excitonic Bose-Einstein condensate can be observed experimentally. Our results indicate the importance of the many-body effects in exploring the optical performance of novel GaN optoelectronic nanodevices.

One of the holy grails of the photon upconversion is to convert near infrared photons to high energy photons in the ultraviolet or violet spectrum. The solar panel at sea level is around 50%[2] low energy infrared photons that current solar panels do not absorb. By utilizing the strong absorption of inorganic nanocrystals (NC), and the ability of conjugated organic emitters to undergo triplet-triplet annihilation (TTA), a hybrid tunable system can be designed with high upconversion Quantum Yields (QYs). A thin layer of this upconversion system may potentially improve solar panel efficiency beyond the Shockley Queisser limit of 30%[1]. Here, the organic emitter of interest is perylene. Perylene has many qualities that make it a promising emitter, such as a high fluorescence QY, a low-lying triplet energy state and fluorescence in the violet wavelengths. However, these high fluorescence QYSs are only observed in dilute solvent, and perylene needs to be tightly bound to the NC surface for efficient energy transfer. In this poster, we address the first problem with bulky substituents on perylene to increase solubility and minimize excimer formation. As for the second limitation, we investigate the covalent binding of perylene to CdSe NCs of various sizes for experimental evidence of the Marcus inverted regime. Information about the relationship between the driving force for triplet energy transfer and its rate will help design better ligands once the reorganization energy, or the coupled vibrations that participate are identified.

Silicon nanowires (SiNW) exhibit unique opto-electronic properties originating from 1-D confinement. All opto-electronic properties: bandgap, charge carrier relaxation rates, and electron nonradiative lifetimes all are influenced by continuous sampling of momentum in growth direction. Here, motivated by our previous studies, we show that the electron relaxation time in <100> SiNW is longer than in <111> SiNW.

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ES19.07.05

Photostimulated Auger Processes in Carbon Nanotubes

Rohit B. Choudhury, Naval Research Laboratory, Washington, District of Columbia, United States.

Carbon nanotubes possess unique electronic band structures that make them ideal for applications ranging from transistors to field emitters. The study of electronic processes in CNTs is of great interest since it can lead to new insights into fundamental physics. The Auger process in semiconductors is a competing non-radiative decay channel that can lead to increased losses in high-power applications. In this study, we present photostimulated Auger processes in carbon nanotubes.

ES19.07.06

Singlet Fission in a Hybrid PbS Nanocrystal-Diphenylhexatriene System

Helen M. Thayer, Carter S. Gerke, Zhiyuan Huang and MingLee Tang; Chemistry, University of California, Riverside, Riverside, California, United States.

Solar cell efficiency could potentially be increased by exceeding the Shockley-Queisser limit through singlet fission. The Shockley-Queisser limit on photovoltaic efficiency is the theoretical maximum efficiency of a p-n junction given our sun. It states that nearly more than half of the light energy incident on a conventional single junction photovoltaic material is not converted to electrical energy. Some of this lost energy could be harvested through singlet fission. Here, inorganic colloidal PbS nanocrystals (NC) are used to harvest the energy from triplet excitons generated by organic 1,6-diphenyl-1,3,5-hexatriene (DPh). In DPh, singlet fission occurs efficiently, whereby an excited photon creates a singlet state that splits into two triplet states—one in the original chromophore and one in a neighboring chromophore. The energy transfer is known as the Dexter process, which is a simultaneous, correlated transfer of charge or energy from a donor to an acceptor non-radiatively. In this work, DPh is the donor while PbS is the acceptor, and Dexter transfer is enhanced by covalently attaching both species to promote wavefunction overlap between donor and acceptor. Synthesis of soluble DPh derivatives with specific functional groups that allow DPh to bind to PbS allow the surface density of molecules on nanocrystals to be controlled. Specifically, phosphonic acid and carboxylic acid functional groups are designed to bind the DPh to the surface of the PbS NC. Energy transfer from DPh to PbS characterized by steady-state and ultrafast absorbance and emission measurements will be presented.

SESSION ES19.08: Photophysical Properties: from the Bulk to the Nanoscale

Session Chairs: Kathryn Knowles and Wajih Ma

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 132 A

8:00 AM -ES19.08.01

Halide Perovskites Bulk vs. Nanoparticles—What is different? What is similar?

Ivan Mora-Sero; Universitat Jaume I, Castello de la Plana, Spain.

Halide perovskites are receiving a huge attention in the recent few years. Undoubtedly this attention is mainly due to the outstanding power conversion efficiencies, surpassing 23%, reported for photovoltaic devices, fabricated with polycrystalline films from low cost techniques. The great success of halide peroviskites boosted also the interest on the nanoparticles (NPs) of these materials. Perovskite NPs are also generating a huge interest as relative easy preparation methods yield a simple core structure, without need for passivating shells, reach photoluminescence quantum yield (PLQY) higher than 90%. This remarkable PLQY points to low non-radiative recombination and consequently shows excellent potential for the development of solar cells and optoelectronic devices. In this talk I show the interest of perovskite NPs in the development of different optoelectronic systems and analyze the similarities and differences with standard bulk perovskite thin films. Interestingly the use of NPs can help to overcome some limitations of bulk perovskites stabilizing new interesting crystalline phases or avoiding mixed halide ion migration. In addition, the interaction of perovskites with other materials can provide useful synergies and their potentialities commented.

8:30 AM -ES19.08.02

Subpicosecond Photoionization of Mn-Doped CdSe Quantum Dots Mediated by Spin-Exchange Auger Interactions

Rohan Singh, Wenyong Liu, Jaehoon Lim, Istvan Robel and Victor Klimov; Los Alamos National Laboratory, Los Alamos, New Mexico, Los Alamos, New Mexico, United States.

Diluted magnetic semiconductors (DMS), especially those containing Mn dopants, have been the subject of numerous studies [1]. A key property of these materials is strong interactions between electronic states of a semiconductor host and Mn dopants mediated by spin-exchange interactions [2, 3]. An interesting aspect of these interactions is their influence on multicharge Auger-type phenomena. In the case of Mn-doped II-VI DMSs, the spin-exchange Auger effect has been invoked to explain highly efficient excitation transfer from a semiconductor to a Mn ion leading to characteristic emission via the internal $^{1}T_{1} \rightarrow ^{3}A_{1}$ transition of a 3d electron. This effect has been observed in both bulk and quantum dot (QD) forms of II-VI DMS materials [1, 4]. Previous studies also indicate that the reverse Auger process whereby the Mn excitation is transferred to the conduction-band electron is also highly probable [5]. In particular, Auger de-excitation was cited to rationalize Mn-emission quenching by injected electrons [6]. Furthermore, there are several direct observations of hot Auger electron produced by this process [7, 8]. Despite the initial indications of a considerable strength of exchange interactions in Mn-doped II-VI QDs, the quantitative understanding of this effect is still lacking. The purpose of the present study is to quantify temporal characteristics of Auger-mediated exchange of excitations between the magnetic ion and the semiconductor by conducting femtosecond transient absorption (TA) measurements of Mn: CdSe QDs. Using low-intensity (sub-single exciton) near band-edge excitation (515 nm), we are able to resolve both “forward” transfer of a band-edge exciton to a Mn ion as well as “backward” transfer. We find that the direct transfer takes place on a ca. 100-fs timescale. The rate of the back transfer, on the other hand, strongly (exponentially) depends on the energy difference between the Mn $^{1}T_{1} \rightarrow ^{3}A_{1}$ transition and the QD band gap, exhibiting a thermally activated behavior. Furthermore, in the case of above-band-gap excitation (343 nm) and high pump intensities (multielectronic regime), we detect the excitation of a “hot” electron from the QD to an external “vacuum” state accompanied by de-excitation of the Mn ion. This indicates an extremely strong exchange coupling of the excited Mn d-d transition to the intraband QD transition, which leads to sub-ps Auger-assisted reexcitation of the “hot” electron prior to its relaxation to the band edge. As a result, the energy transferred from the Mn ion adds up with the kinetic energy of the unrelaxed carrier, which allows it to escape from the QD.
Colloidal semiconductor quantum dots (QDs) have been envisioned as promising materials for application in traditional light-emission devices and prospective single-dot light sources. While QD displays have already entered the market place, realization of single-dot applications still requires overcoming several challenges including elimination of strong spectral fluctuations at the individual-QD level. Recently, there has been considerable progress in suppressing intensity fluctuations by encapsulating an emitting core (usually CdSe) into an extra-thick protective shell (commonly CdS) [J. Am. Chem. Soc. 130, 5026, 2008, Nat. Mater. 7, 659, 2008]. Despite nearly “blinking-free” emission intensity, these dots, however, still show considerable fluctuations in both emission energy and linewidth. Here we demonstrate a new class of QDs that overcome both deficiencies. In these dots, the CdSe core is enclosed into a compositionally graded, asymmetrically-strained Cd$_{1-x}$Zn$_x$Se shell [Nat. Mater. 17, 42, 2018]. These structures exhibit a highly stable emission energy (~0.5 meV standard deviation versus ~10 meV in CdSe/CdS QDs) and an unprecedentedly narrow, subthermal room-temperature linewidth (~20 meV). These unusual properties are derived from unique structural features of these QDs, which leads to strong suppression of exciton-phonon coupling and reduction in propensity for random photoccharging. The remarkable spectral characteristics along with fast emission rates (~1/15 ns) and high emission quantum yields (up to ~85%) make these novel structures well suited for practical realization of single-dot light sources.

**9:30 AM ES19.08.05**

**Colloidal Synthesis of Ternary and Heterostructured 2D Semiconductor Nanocrystals**

Alina Schimnich; UC San Diego, La Jolla, California, United States.

Colloidal semiconductor nanocrystals have played an important role in the search for and development of next-generation technologies, owing largely to their potential for solution processability and size-tunable optical properties. Two-dimensional semiconductor nanocrystals have recently gained much attention for their unique, layer-dependent electronic, optical and magneto-optical properties, making them attractive for myriad applications in catalysis, energy conversion and optoelectronic devices. Although accessing lateral quantum confinement in these materials may be difficult, their properties may be tuned via other strategies including the formation of heterostructures or multinary alloys. Herein we present colloidal syntheses of heterostructures based on binary and ternary two-dimensional semiconductors such as WSe$_2$ and Cu$_2$WSe$_4$. These syntheses take advantage of nanocrystal conversion chemistry to access otherwise difficult compositions and structures.

**10:00 AM BREAK**

**SESSION ES19.09: Hybrid Materials for Energy Conversion II**

Session Chairs: Mark Wilson and Nobushiro Ysnai

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 132 A

**10:30 AM ES19.09.01**

**Mixed-Anion Semiconductors for Photocatalytic Water Splitting Under Visible Light**

Ryu Abe; Graduate School of Engineering, Kyoto University, Kyoto, Japan.

Photo-induced water splitting using semiconductor photocatalysts has attracted considerable attention for producing H$_2$ as a clean energy carrier, while the effective utilization of visible light is imperative to achieve the desired efficiency for practical applications. [1] Recently, mixed-anion compounds such as oxyanides have been intensively studied as promising candidates since one can expect that higher energy p orbitals of non-oxide anions (e.g., N-2p) elevate their valence band maximum (VBM) values. Unfortunately, most of them are subject to facile self-oxidation by photogenerated holes, while highly dispersed cocatalyst particles certainly improve the stability of some oxyanides. [2] We have recently demonstrated that Silvan-Aurivillius type perovskite oxycalixes such as Bi$_2$NbO$_6$Cl can stably and efficiently oxidize water to O$_2$ under visible light without any surface modifications, and also exhibits a stable Z-scheme water splitting when coupled with a H$_2$-evolving photocatalyst. [3] It was revealed that the VBMs of these materials consist mainly of O-2p orbitals, instead of Cl-3p (or Br-4p), but their positions are much more negative than those of conventional oxides. [4, 5] Thus, they possess narrow bandgaps for visible light absorption as well as sufficiently negative CBMs for water reduction. DFT calculation visualized a fairly strong hybridization between the Bi-6s and O-2p orbitals, which can explain why the O-2p orbitals are elevated in energy, combined with the result on Madelung site potential analysis that can rationalize the origin of high energy of O-2p orbital in these materials. Since O-2p orbitals are known to be relatively stable, generated holes populated at the O-2p orbitals will not lead to self-decomposition but to oxidize water. These results could provide new strategies for developing durable photocatalytic materials for water splitting under visible light, by manipulating the interaction between post-transition metal s orbitals and O-2p orbitals.


**11:00 AM ES19.09.02**

**Size Dependent Donor and Acceptor Pair Recombination in Colloidal Silicon Quantum Dots**

Hiroshi Sugimoto and Minoru Fujii; Kobe University, Nada Kobe, Japan.

Defining the optoelectronic features of semiconductors quantum dots (QDs) by introducing a few impurity atoms is a novel way to tailor new functionalities towards the photonic applications. Formation of localized impurity states in the energy gap enables to engineer the emission properties exceeding the range that can be achieved by size and shape control. In fact, attempts to exploit emission properties of QDs by impurity doping have initiated for compound semiconductor such as Cu or Ag-doped CdSe QDs and Mn-doped ZnSe QDs. In contrast to the great advancements in compound semiconductors, impurity-doping in Si QDs is still at the fundamental level despite its importance in optoelectronics and biophotonics applications.

In this work, we present the development of colloidal Si QDs codoped with boron (B) and phosphorus (P) [1,2] The codopants introduce donor and acceptor levels in the band gap of Si QDs and thus enable the optical transition with the energy below bulk Si bandgap (~1.1 eV). The emission energy is tunable in the range of 0.9-1.8 eV [1] which is optimal for...
carrier multiplication facilitated solar cell power conversion. In this work, to extract the information on impurity-induced effects quantitatively, we apply the size-purification process for lifting the size inhomogeneity. We have succeeded in preparing almost monodispersed codoped Si QDs. In the size-purified and selected QDs, we determine the degree of doping-induced shrinkage of the optical band gap over a wide size range. From the comparison of the optical data with recent results on single QD analyses including scanning tunneling spectroscopy, we discuss the size dependence of donor-acceptor (D-A) states in Si QDs. We present the number of D-A pairs in a QD in a wide size range by the comparison with theoretical calculation. In addition, we investigate the decay dynamics of D-A pair recombinations as a function of emission energy and the QD size. The results indicate that around 5.5 nm is a critical dimension, where the behavior of D-A pairs in a Si QD changes drastically. Finally, we demonstrate the potential of codoped Si QDs as near-IR luminescent probes in bio-imaging. These results demonstrate that codoped Si QDs offering efficient below 1.1 eV emission could be leveraged for not only QD-based solar energy conversion but also bio-imaging operated in the transparent window of biological tissue (700-1300 nm).


11:30 AM ES19.09.03

Excited-State Charge-Transfer Reactivity of QD-Linker-Metal Oxide Heterostructures with Amine-Bearing Bifunctional Molecular Linkers

Natalia Rivera-Gonzalez and David Watson; Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, United States.

Semiconductor quantum dots (QDs) are intriguing harvesters of light and donors of excited charge carriers for solar energy conversion. To exploit this potential requires the localization of QDs at interfaces with appropriate energetic offsets for charge separation. We and others have reported the use of mercaptalanoic acids and related thiol-bearing linkers to tether organic-capped CdS and CdSe QDs to nanocrystalline TiO2 thin films. Electrons can be transferred efficiently from photoexcited QDs to the TiO2 substrate through mercaptoalanoic acid linkers. Unfortunately, adsorbed thiolates can accept valence-band holes efficiently from photoexcited QDs, reducing the distance between photogenerated electrons in TiO2 and holes in the thiolates, and additionally promoting the deleterious oxidative degradation of linking ligands.

To address this issue, we are exploring the use of amine-bearing linkers as alternatives to the thiolated linkers. Amines are attractive because they can coordinate to cadmium chalcogenide QDs without accepting holes, which maximizes the spatial separation of charge carriers following electron transfer to metal oxides. In addition, amines enhance band edge emission, shifting trap-state emission to higher energy and eliminating electron-hole recombination pathways. This presentation will focus on (1) synthesis of the heterostructures via both in situ and ex situ synthetic approaches, which differ in the ordering of surface-functionalization events, and (2) spectroscopic and photoelectrochemical characterization of excited-state charge-transfer within the heterostructures. In ex situ synthesis, CdSe QDs are first functionalized with the linking ligand, and these linker-functionalized CdSe QDs are then attached to the metal oxide. We have developed a two-step ligand-exchange mechanism to obtain para-aminobenzonic acid (PABA)-functionalized CdSe QDs by using oleate-capped CdSe QDs as the starting QDs and pyridine-CdSe QDs as the intermediate QDs. We subsequently optimized the attachment of PABA-CdSe QDs to TiO2. Time-correlated single-photon-counting of QD-TiO2 heterostructures reveal charge-transfer induced dynamic quenching of emission from QDs with excited-state electron-transfer rate constants on the order of 10^9 s^-1. This presentation will emphasize insights into the mechanism and time scale of photoinduced electron transfer at QD-TiO2 interfaces as a function of interfacial properties and the mechanism (in situ or ex situ) by which heterostructures were prepared. Results of ongoing photoelectrochemical experiments on QD-sensitized solar cells will also be presented.


11:30 AM ES19.09.04

Molecularly-Localized Energy of Exciton Confined in the One-Dimensional Nanostructures of Single-Walled Carbon Nanotubes

Tomohiro Shiraki1-2, 1Department of Applied Chemistry, Kyushu University, Fukuoka, Japan; 2ICNER, Kyushu University, Fukuoka, Japan.

Single-walled carbon nanotubes (SWNTs) are one dimensional (1D) nanomaterials with a diameter of ca. 1 nm and a length of a few hundred nm or ~μm. The tubular structures are composed of rolled up single graphene, and the rolled-up manner, which is identified by chiral indices, determines their optical and electronic properties, such as metallic and semiconducting features. The semiconducting SWNTs show photoluminescence (PL) in near infrared (NIR) regions through a relaxation process of exciton generated by photo-excitation. Single-walled carbon nanotubes (SWNTs) are one dimensional (1D) nanomaterials with a diameter of ca. 1 nm and a length of a few hundred nm or ~μm. The tubular structures are composed of rolled up single graphene, and the rolled-up manner, which is identified by chiral indices, determines their optical and electronic properties, such as metallic and semiconducting features. The semiconducting SWNTs show photoluminescence (PL) in near infrared (NIR) regions through a relaxation process of exciton generated by photo-excitation. SWNTs have different electronic structures by the modification, and can trap the migrating excitons and then emit PL efficiently, giving PL intensity enhancement with wavelength shifts. Recent studies are revealing that doped site structures of the IF-SWNTs relate to the resultant PL functions. This presentation reports new findings based on our molecular design approach to create structurally-designed doped sites, in which unique PL properties appear based on the functionalized molecules.[1-6] For example, bisaryldiazonium salts (2Dz) were synthesized and used for the modification of SWNTs with (6,5) chiral index (lf-SWNTs/2Dz), providing new red-shifted PL.[1] Namely, the PL peak appeared at 1256 nm which was significantly red-shifted than those of non-functionalized SWNTs (985 nm) and mono-functionalized SWNTs (lf-SWNTs/1Dz, 1129 nm). In another project, substituted aryl isomers were introduced as a moiety of the doped site structures of lf-SWNTs. The observed PL was varied with strong dependence on the isomeric substituent positions.[3] Thus, these molecular structure-dependent spectral changes are expected to modulate the NIR PL in a wide wavelength range. As another function of the IF-SWNTs, dynamic wavelength shifting is achieved through creation of the doped sites that selectively bind molecules and ions.[2, 5, 6] The local binding occurred by employing molecular recognition motives for the doped site structures. The first example was phenylboronic acid-modified lf-SWNTs that showed PL in situ and ex situ and in situ synthesis, CdSe QDs are first functionalized with the linking ligand, and these linker-functionalized CdSe QDs are then attached to the metal oxide. We have developed a two-step ligand-exchange mechanism to obtain para-aminobenzonic acid (PABA)-functionalized CdSe QDs by using oleate-capped CdSe QDs as the starting QDs and pyridine-CdSe QDs as the intermediate QDs. We subsequently optimized the attachment of PABA-CdSe QDs to TiO2. Time-correlated single-photon-counting of QD-TiO2 heterostructures reveal charge-transfer induced dynamic quenching of emission from QDs with excited-state electron-transfer rate constants on the order of 10^9 s^-1. This presentation will emphasize insights into the mechanism and time scale of photoinduced electron transfer at QD-TiO2 interfaces as a function of interfacial properties and the mechanism (in situ or ex situ) by which heterostructures were prepared. Results of ongoing photoelectrochemical experiments on QD-sensitized solar cells will also be presented.

Colloidal quantum dots can be used to engineer band degeneracies and connectivities that may result in fundamentally new solid-state physics. Here, a compact fluorinated ligand, trifluoromethylthiolate, is used to functionalize PbS semiconductor quantum dots (QDs). The electron-withdrawing fluorinated shells allow band energies to be engineered to introduce a depletion layer in a QD thin film and thus improve charge transport in a device. Importantly, the self-assembled superlattices have strong electronic coupling between constituent QDs arising from the short interdot distances. Thin-film transistor measurements show current staircases, reminiscent of Coulomb blockades recorded at 4K on single particles, despite the fact that our measurements are performed at RT on micron-sized devices over 1000-10000 QDs. This talk will discuss the charge transport in these PbS QD thin films.

Formation of Electronically and Chemically Passive Termination on PbSe Quantum Dot Superlattices

Colloidal synthesized nanocrystals are attractive ‘designer atoms’ that can be used to engineer band degeneracies and connectivities that may result in fundamentally new solid-state physics. Here, a compact fluorinated ligand, trifluoromethylthiolate, is used to functionalize PbS semiconductor quantum dots (QDs). The electron-withdrawing fluorinated shells allow band energies to be engineered to introduce a depletion layer in a QD thin film and thus improve charge transport in a device. Importantly, the self-assembled superlattices have strong electronic coupling between constituent QDs arising from the short interdot distances. Thin-film transistor measurements show current staircases, reminiscent of Coulomb blockades recorded at 4K on single particles, despite the fact that our measurements are performed at RT on micron-sized devices over 1000-10000 QDs. This talk will discuss the charge transport in these PbS QD thin films.

Achieving ordered macroscopic crystal-like assemblies has been in the focus of researchers for years, since it would allow for exploitation of the quantum confinement-based electronic properties with tunable dimensionality, but was considered by many as a mere academic game as the polidispersity of colloidal systems should have hindered the emergence of collective behaviors. Lead-chalcogenide colloidal quantum dots show especially strong tendencies to self-organize into 2D superlattices with micron-scale order, making the array fabrication fairly simple. However, most work concentrates on the fundamentals of the assembly process, and none have investigated the electronic properties and their dependence on the nanoscale structure induced by different ligands. In my presentation, I will show the formation of large arrays of colloidal quantum dots and the dependence of the nanostucture, the optical and the electronic transport properties of the superlattice on chemical treatment (ligand exchange) performed. Transistors with average two-terminal electron mobilities of 13 cm^2/VS and contactless mobility of 24 cm^2/VS are obtained for small area superlattice FETs [1]. Such mobility values are the highest reported for CQD devices wherein the quantum optical is substantially still present, and are comparable to those reported for heavy sintering. The next step to make an electronic metamaterial which could be highly relevant for optoelectronics, is to use the surface of the quantum dots to change their stoichiometry and tune their transport properties. I will show that more than two orders of magnitude improvement in the hole mobility, from below 10 to above 0.1 cm^2/VS, by substituting iodide ligands with sulfide, while keeping the electron mobility stable (~1 cm^2/VS) were achieved [2]. The considerable mobility, the possibility of tuning their transport properties with the simultaneous preservation of the optical band gap displays the vast potential of colloidal QD superlattices for optoelectronic applications.

[1] Balazs, D.M.; Matysiak, B. M.; Momand, J.; Shulga, A. G.; Ibáñez, M.; Kovalenko, M.V.; Kooi, B. J.; Loi, M. A.: Electron Mobility of 24 cm^2V-1s-1 in PbSe Colloidal-Superlattices for optoelectronic applications. The considerable mobility, the possibility of tuning their transport properties with the simultaneous preservation of the optical band gap displays the vast potential of colloidal QD superlattices for optoelectronic applications.


Towards Electronic Minibands—Superlattices with PbS QDs in a Fluorinated Matrix

PbS colloidal quantum dot colloids are attractive systems for optoelectronic applications due to their quantum confinement-induced optical properties and electronic transport properties. The electron-withdrawing fluorinated shells allow band energies to be engineered to introduce a depletion layer in a QD thin film and thus improve charge transport in a device. Importantly, the self-assembled superlattices have strong electronic coupling between constituent QDs arising from the short interdot distances. Thin-film transistor measurements show current staircases, reminiscent of Coulomb blockades recorded at 4K on single particles, despite the fact that our measurements are performed at RT on micron-sized devices over 1000-10000 QDs. This talk will discuss the charge transport in these PbS QD thin films.

3:20 PM *ES19.10.11

Photocontrollable Optoelectronic Devices Consisting of an Assembly of Photochromic Compounds

In molecular electronics, photochromic compounds are considered to be promising candidates for optoelectronic molecular electronic devices. In diarylethenes the π-system of the two aryl rings is separated in the open-ring isomer, while the π-system is delocalized throughout the molecule in the closed-ring isomer. The magnetic interaction in the open-ring isomer is inherently weak from the disjoint nature of the n-system. On the other hand, in the closed-ring isomer resonant closed-shell structure brings about strong magnetic interaction. Based on this idea we have demonstrated that the exchange interaction between two nitrolyl nitroxide radicals connected by a diarylethene unit was photowitching reversally along with photoluminescence from the measurement of the magnetic susceptibility, ESR signal intensity, and ESR signal splitting. By preparing the diarylethene-gold nanoparticles network made of diarylethene dithiophenol, the completely reversible photoswitching of conductance through the organic molecule has been achieved. Diarylethenes, which have same core structures but have different positions of thiol groups that are bound to gold nanoparticles, were prepared. In one diarylethene, which has two thiol groups at the positions equivalent to 5,5'-positions of di(3-thienyl)ethene, but in the other diarylethene, which has two thiol groups at 2- and 5-positions of one of the 3-phenyl group. The gold nanoparticle networks of these diarylethenes were prepared and the charge in conductance was measured upon alternate irradiation with UV and visible light. For two diarylethenes, the direction of the photoswitching was opposite, reflecting the difference in the π-connectivity. The result suggests that the topology of π-conjugation between electrodes is the decisive factor in the conductance of gold nanoparticle network (J. Phys. Chem. Lett. 2016, 7, 2113).

Optical switching organic field-effect transistors (OFETs) provide a new direction for optoelectronics based on photochromic molecules. However, the patterning of OFETs is the decisive factor in the conductance of gold nanoparticle network (J. Phys. Chem. Lett. 2016, 7, 2113).
difficult because conventional fabrication processes, including lithography and ion etching, inevitably cause severe damage to organic molecules. We demonstrated laser patterning of one-dimensional (1D) channels on an OFFET with a photorefractive diethylenetriamine (DAE) layer. A number of 1D channels can be repeatedly written and erased in the DAE layer by scanning focused ultraviolet and visible light laser beams and the conductance of the 1D channel can be controlled by the illumination conditions. This result will open new possibilities for realizing various optically reconfigurable, low-dimensional organic transistor circuits (Nano Lett. 2016, 16, 7474).

3:00 PM BREAK

3:30 PM *ES19.10.05

Spectral Engineering for Narrow-Band Colloidal Quantum Dot Optoelectronics Susanna M. Thon, Ebuka S. Arinze, Botong Qiu, Yida Lin, Arlene Chiu, Yan Cheng and Lulin Li; Electrical and Computer Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Colloidal quantum dots (QD)s are attractive materials for energy harvesting and sensing applications because they combine flexible, low-cost solution-phase synthesis and processing with internalized infrared. PbS-based QDs with band gaps that can be tuned throughout the near and mid-infrared wavelengths via the quantum confinement effect are a promising materials system for photovoltaics and photodetectors that harvest non-visible radiation. The ability to achieve true wavelength-selectivity for applications such as transparent and multijunction photovoltaics, narrow-band photodetectors, and tailored emission sources has been lacking to this point, however. Here, we discuss several new strategies for achieving spectral selectivity and color-tuning in QD thin films. We use thin layer interference engineering and multiojective optimization algorithms to design devices with controlled absorption, reflection, and transmission profiles while simultaneously maintaining high current in QD solar cells. We also discuss an alternate method for achieving spectral selectivity in optoelectronic thin films: the use of photonic band engineering within the absorbing region of a semiconductor in which resonant states are strongly coupled to the external reflectivity and transmission spectra. Using optical models and proof-of-principle experiments, we show that photonic bands can be maintained in a new regime: with strongly absorbing materials. We further showed that this effect can be used as a tuning mechanism for enabling spectrally-selective absorption and transmission of light. We demonstrate the viability of this method in experiment by making new materials based on photonic crystal structures consisting of PbS QDs infiltrated into an inverse opal structure provided by self-assembled dielectric nanospheres. This work represents a new spectral tuning mechanism and should additionally enable applications such as current-matching in multi-junction solar cells and miniaturized wavelength-selective photodetectors for sensing applications.

4:00 PM ES19.10.06

I-III-VI: Semiconductor-Based Colloidal Nanorod Heterostructures for Multifunctional Optoelectronics Nuri Ob1, Logan Keating2, Gryphon Drake2 and Moonsub Shim2; 1Materials Science and Engineering, Hanyang University, Seoul, Korea (the Republic of); 2Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Beyond the conventional core/shell structures of colloidal semiconductor nanocrystals, the incorporation of active heterojunctions in emerging anisotropic structures has brought about new capabilities for optoelectronic applications. Recently, it has been demonstrated with double-heterojunction nanorods to independently control over electron and hole injection/extraction processes, allowing improved electroluminescence and simultaneous photodetection/photovoltaic capabilities. However, most efforts thus far have been made in Cd-based II-VI materials that face severe usage restrictions in consumer products. Hence, expanding the composition space for colloidal nanocrystal heterostructures of varying shapes should facilitate practical implementation. One of the interesting candidates is I-III-VI: compound semiconductors, which have similar crystal structures as the II-VI materials. Above all, much of the chemistry developed for II-VI nanocrystal heterostructures can be adapted for ternary compounds. However, the direct formation of I-III-VI: based nanocrystal heterostructures has rarely been reported due to the compositional complexity. Even the previous approaches via sequential cation exchange from II-VI based dot-in-rod structures have several limitations including non-selectivity for co-existing cations and formation of undesired defects and impurities. Here, we examine and develop synthesis of colloidal I-III-VI: nanorods and subsequent epitaxial growth of heterostructures. Starting with CuGaS2/ nanorods, sawtooth-shaped CuGaS2/CuInS2 and CuGaS2/CuInSe2 nanorod heterostructures (NRHs) are achieved with subtle variations in shape caused by differences in lattice mismatch. Growth of ZnS shell on CuGaS2/CuInSe2 NRHs leads to enhanced PL and other interesting/useful optical properties, including large pseudo-Stokes shift and charge separation within the NRHs. Changing the final stoichiometry of ZnSe to ZnSe leads to similar features as those of ZnSe shell initially but continued growth results in unusual brush-like heterostructures. Building on our synthetic strategy to extend anisotropic nanocrystal growth to introduce the multiple active heterojunctions should pave the way for developing application-specific design and synthesis of multifunctional optoelectronic materials.

4:15 PM ES19.10.07

Direct Measurement of Charge and Electric Field in Quantum Dot Light-Emitting Diodes Han Zha1, Giovanni Azzellino1, Matthew Chua1, Jason Yoo1, Mounig Bawendi1 and Vladimir Bulovic1; 1Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Colloidal quantum dot light-emitting diodes provide a highly promising platform for efficient, color-tunable, and stable solid-state lighting and display technologies. A quantitative understanding of its device physics is required to achieve high efficiency across a large range of brightness and emission wavelength. While studies have demonstrated the detrimental effects of excess charge carriers, large electric field, and leakage current on device efficiency, these internal state variables have never been directly measured. This leads to challenges in validating quantitative physical models that relate device parameters, internal state variables, and device performance.

In this work, we perform differential absorption measurements using a sub-millisecond laser to directly measure both charge density and electric field strength in a working QD-LED at high current density (up to 1000 mA/cm2) and output brightness. We observe that charge density in the quantum dot film drastically increases with bias before eventually reaching a plateau, a trend that is consistent with multiple injection regimes of charge balance characterized by different efficiency loss mechanisms. We show that the amount of injected charge can be controllably adjusted from 0.5 electrons per QD to 2 electrons per QD by simply varying the thickness of the quantum dot layer by less than 15nm. This leads to differing degrees of loss through Auger recombination and can offer insights into the dynamics of excitation formation at the interface of the quantum dot film and neighboring semiconducting transport layers. Finally, we use independent measurements of charging and electric field strength to characterize the transition from interface limited conduction to space-charge limited conduction. These results provide a significant improvement in the quantitative understanding of the operation QD-LEDs and can lead to better rationalization of device performance.

4:30 PM ES19.10.08

Low-Threshold Optically Pumped Lasing in LED-Like Stacks Based on Colloidal Quantum Dots Heojung Kim1, Young-Shin Park1,2 and Jae-Hoon Lim1,3; 1Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 2Center for High Technology Materials, The University of New Mexico, Albuquerque, New Mexico, United States; 3Department of Chemical Engineering & Department of Energy System Research, Ajou University, Suwon, Korea (the Republic of).

Colloidal quantum dots (QDs) have gained considerable attention as promising candidates for realizing solution-processible lasing devices including laser diodes. Important milestones on the way towards a QD-based laser technology have been recent demonstrations of low-threshold optically pumped devices operating under pulsed (Nano Lett. 15, 7319, 2015) and continuous-wave (Nature 544, 75, 2017) excitation. However, demonstration of lasing with electrical pumping remains challenging because of fast optical gain decay via intrinsic nonradiative Auger recombination and thermal instabilities in the QD gain medium under high excitation conditions. Recently, we demonstrated a population inversion and optical gain under electrical pumping in a QD light-emitting diode (QD-LED) using continuously graded QDs with suppressed Auger recombination and employing a current focusing architecture which allowed for achieving high current densities of (~20 A cm2) without device overheating (Nat. Mater. 17, 42, 2017). The next step towards an electrically pumped laser diode is integration of an optical cavity into the QD-LED structure. In this study, we demonstrate optically pumped laser in a multilayer waveguide structure whose architecture is similar to that of a standard QD-LED. A one-dimensional periodic distributed feedback (DFB) grating was imprinted onto an ITO transparent electrode using laser interferometric lithography. In order to improve optical mode confinement within the gain-active QD layer, we engineered the refractive index of ITO so as to reduce the mode leakage into the underlying electrode. The developed structure exhibited strong lasing performance (~630 nm) with optical feedback provided by the in-plane 2nd order scattering and out-of-plane light outcoupling due to the 1st order scattering. Despite the presence of a “lossy” conductive electrode, our fully optimized structures exhibited a very low lasing threshold of ~5.5 μJ/cm2 which was on-a-par with the lowest thresholds reported for QD lasers of any type (Nano Lett. 15, 7319, 2015). As the next step, we employed a zinc oxide (ZnO) interlayer, which was commonly used in QD-LEDs as an
electron-transport layer (ETL), and investigated lasing performance of an ITO-DFB/ZnO/QD multilayer structure. We found that the QD DFB laser with ZnO still exhibited excellent lasing performance with a low threshold (~5.7 µJ/cm²) achieved upon full optimization of all elements of our multilayer stacks. Finally, we deposited 4,4',4''-tris(carbazol-9-yl)-triphenylamine (TCTA) as a hole-transport layer (HTL), on top of the QD layer to form a nearly complete LED stack comprised of transparent electrode/ETL/QD/HTL. Importantly, the deposition of TCTA did not distort optical properties of the DFB resonator, which retained a well-defined photonic gap. As a result, the developed device stacks showed good lasing performance although with a moderately increased threshold of ca. 17 µJ/cm², which was expected to become lower upon device optimization. The results of this work along with the recent demonstration of optical gain in QD-LEDs reaffirm the feasibility of solution processible QD-based laser diodes.

**4:45 PM ES19.10.09**

**Bridge the Gap Between Photoluminescence and Electroluminescence of Colloidal Quantum Dots**

Xingliang Dui; Zhejiang University, Zhejiang Province, China.

Colloidal Quantum dots (QDs) are a unique class of emitters with size-tunable emission wavelengths, saturated emission colors, near-uniform luminescence efficiency, inherent photo- and thermal-stability and excellent solution processability. The superior photoluminescence properties of QDs have already initiated applications as back-lighting for liquid-crystal displays to improve color gamut, which rapidly grows into multi-billion dollar business. Fully exploiting the superior luminescence properties of QDs in electroluminescence devices promises low-cost, large-area, flexible and yet high-performance LEDs, which shall revolutionize display and solid-state lighting. For the past two decades, a lot of efforts concentrated on materials and device structures of quantum dot light emitting diode (QLED) have been paid to improve devices performance. But the efficiency and lifetime of QLEDs are far behind the requirements for practical applications. Clearly, there is a performance gap between photoluminescence and electroluminescence of QDs. To bridge the photoluminescence-electroluminescence gap of QDs, in-depth understanding of the formation and decay processes of electrically excited states in QDs is urgent and indispensable. In the past few years, we designed a conceptually new device structure containing an ultrathin insulating layer for QLEDs and integrated almost functional layers by solution process. The insulating layer modulate the electron injection to optimize charge balance and maintain superior emissive properties of QDs, forming efficient exciton generation and radiative decay cycle. Finally we realized the state-of-the-art solution-processed red LEDs with sub-bandgap turn-on voltage (1.7 V), record efficiency (EQE > 20%) and outstanding operational stability (~10⁵ hours @100 cd m⁻²). The two functions of the insulating layer can be decoupled and addressed separately. Suppressing exciton quenching at electron-transport-layer (ETL)/QDs interface, which is identified as being obligatory for high-performance devices, is achieved by adopting ZnₓMgᵧ₋ₓO nanocrystals, instead of ZnO nanocrystals, as ETLs. Optimizing charge balance is readily addressed by other device engineering approaches, such as controlling the oxide ETL/cathode interface and adjusting the thickness of the oxide ETL. Insights revealed by device physics studies further help us to bridge the photoluminescence-electroluminescence gap of QDs, realizing much extended QLED operation stability. These devices show a Tₜₜ operation lifetime of more than 3,500 h at an initial brightness of 1000 cd m⁻² for red LEDs, representing the most stable QLEDs so far. These achievements bring QLED technologies a step closer towards real-life applications.

**SYMPOSIUM ES20**

**TUTORIAL: Young Scientists Tutorial on Characterization Techniques for Thin-Film Solar Cells**

April 22 - April 22, 2019

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* Invited Paper

**TUTORIAL**

**Young Scientist Tutorial on Characterization Techniques for Thin-Film Solar Cells**

Monday Morning, April 22, 2019

PCC North, 100 Level, Room 132 B

This tutorial is intended for young researchers (students and post-graduates within 3 years of degree completion) who are active in the field of thin-film solar cells and would like to learn the fundamentals of characterization methods that are being used in research and development of these materials and devices. All presentations will be given (mostly) by young, yet experienced researchers who are active in the characterization of Si-, III-V-, chalcogenide-, kesterite-, as well as perovskite-based solar cells. Although these materials will be discussed as model systems, the presentations will primarily focus on the characterization and simulation techniques and thus should be of interest to participants from other symposia as well.

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**8:30 AM**

**Electrical Device Characterization and Modeling of Thin-Film Solar Cells**

Mike Scarpulla; The University of Utah

I-V and C-V DC analyses, AC characterization (CV, DLCP, DLTS and related techniques), localized state and band-structure-related responses; simulations using 1D solvers such as SCAPS and extensions to 2D; “hands-on” simulation demonstration.

**10:00 AM BREAK**

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**10:30 AM**

**Soft X-Ray and Electron Spectroscopies: Investigating the Chemical and Electronic Structure of Surfaces and Interfaces**

Dirk Hauschmidt; Karlsruhe Institute of Technology

Introduction to several soft x-ray and electron characterization techniques, including x-ray (XPS) and UV (UPS) photoelectron spectroscopy, inverse photoemission spectroscopy (IFES), x-ray excited Auger electron spectroscopy (XAES), and x-ray emission spectroscopy (XES). The tutorial includes a discussion of experimental requirements, information content, as well as data analysis and interpretation. Examples how the techniques can be used to determine the electronic and chemical structure of surfaces and interfaces in thin-film photovoltaic devices will be given.

**1:30 PM**

**Time-Resolved Terahertz Spectroscopy on Energy Materials**

Hannes Hempel; Helmholtz-Zentrum Berlin für Materialien und Energie

Introduction to measurement, analysis and application of time-resolved terahertz spectroscopy (TRTS). Determination of charge carrier mobility, bulk lifetime and surface recombination velocity demonstrated on the example of perovskites, kesterites and metal oxides. Impact of these key properties on solar cell efficiencies. Comparison of TRTS to alternative measurement techniques.
Introduction to scanning transmission electron microscopy and the accompanying analytical techniques including atomic number contrast annular dark field imaging, electron energy loss spectroscopy (EELS) and Energy Dispersive X-ray spectroscopy (EDX). The focus will be the application of these techniques on understanding structure and composition in solar materials, with examples from CdTe and CIGS solar cells. In addition, state-of-the-art in-situ heating technique will be discussed as a powerful means of understanding solar materials growth.

4:00 PM
Atomistic Modeling of Defects in Materials Kyoung Eun Kweon; Lawrence Livermore National Laboratory

Understanding defects and their roles in determining materials properties. Demonstration on how to compute thermodynamic and kinetic properties of (point) defects and defect complexes, particularly in Cu(In,Ga)Se2. Discussion includes how the atomistic calculations can be used to interpret/understand experimental observations.

SYMPOSIUM ES20

Thin-Film Chalcogenide Semiconductors Photovoltaics
April 23 - April 26, 2019

Symposium Organizers
Shubhra Bansal, University of Nevada, Las Vegas
Nicolas Barreau, Universite de Nantes
Alex Redinger, University of Luxembourg
Mike Scarpulla, The University of Utah

Symposium Support
AVANCIS GmbH
Codex International
First Solar
University of Luxembourg/Fonds national de la recherche (Luxembourg)

* Invited Paper

SESSION ES20.01: Device Modelling
Session Chairs: Stephan Lany and Pawel Zabierowski
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 132 B

10:30 AM *ES20.01.01
Development of an Integrated ACIGS Solar Cell Device Model at MiaSolé Hi-Tech Jeff Bailey, Geordie Zapalac, Dmytro Poplavsky and Rouin Farshchi; MiaSolé Hi-Tech, Santa Clara, California, United States.

Thin-film Ag-CIGS (or ACIGS) solar cells and modules produced by MiaSolé Hi-Tech yield high efficiencies rivaling polycrystalline silicon-based modules but are based on a high-throughput, PVD-based deposition process on flexible stainless steel substrates. The process is unique among thin-film solar manufacturers in that a complete device stack is produced without a vacuum break in less than one hour. Using this manufacturing system, a high level of process control and stability is possible via real-time control of the deposition process.

To continue performance improvements that close the gap between manufacturing material and champion small devices, a better understanding of the fundamental device properties is required. This requires development of a device model that accounts for electrical performance characteristics observed under light and voltage stress over time for comparison to real-world solar cell performance.

Our recent effort to generate a fundamental device model began with employing a wide variety of characterization results from our own measurements, those of our research partners, and features of many CIGS materials that have previously been excluded in prior device models. Additionally, device parameters must be based on actual device measurements and constituents, as heterojunction ACIGS solar cell devices are complex and errors compound quickly. The overall objective was to keep the model as simple as possible and look for generally good agreement among a variety of simulated measurements.

Most of the effort has been devoted to understanding the defect structure of the ACIGS absorber layer. Conventional capacitance-voltage profiling is supplanted in our measurements by high-speed C-V profiling (HSCV) that avoids many complications of transient charge effects in highly defective materials such as ACIGS. An important consequence of these measurements is the discovery that MiaSolé absorber layers (as well as other CIGS devices) can be defined by an acceptor-rich layer (ARL) adjacent to the CdS buffer layer. This ARL has been shown to have profound consequences for device electrical performance, as it can degrade fill factor and reduce efficiency.

The physical basis for the ARL is a matter of some debate. A variation in static shallow acceptor concentration is one possible source, but it predicts neither device metastability nor measured high concentrations of DLTS-visible defects. Charge accumulation at high concentrations of deep acceptors would be possible, but accounts for neither metastability nor carrier capture kinetics observed in DLTS. Instead we hypothesize that V(Se)-V(Cu) divacancy defects are responsible for charge accumulation in the ARL, and their simulated response to light- and voltage-stressing is consistent with our measurements. This hypothesis is qualitatively consistent with positron annihilation spectroscopy (PAS) measurements of our absorber. Predicted shallow acceptor and donor levels of the divacancy also provide an explanation for the long-observed high dopant compensation in CIGS, and at the concentrations predicted by our model, it is possible that the divacancies alone can be used to explain most of the charge and doping profile of the absorber.

Emphasis of the divacancy defect in our device model can guide MiaSolé Hi-Tech to new directions for device improvement that leverage our ability to directly manipulate absorber stoichiometry in our unique thin-film solar manufacturing system.

11:00 AM ES20.01.02
Diagnosing Recombination and Resistive Losses in Thin-Film Chalcogenide Solar Cells Using a Silicon-Inspired Characterization Platform Arthur Onno1, Amit Munshi2,
Spatial Inhomogeneities of Carrier Transport Properties in Polycrystalline Thin-Film Solar Cells

Several characterization techniques are usually performed on a localized region of any material because of convenience in a routine basis. However, lateral non-uniformities in chemical composition, structural defects and even the presence of voids can be found in a polycrystalline solar cell, i.e. CIGS, influencing the local carrier properties of the material. This implies that some of the material properties extracted from local characterization methods may not be representative of the full device performance complicating the correlation between measurements. For example, time-resolved photoluminescence (TRPL) is typically measured locally, and the effective lifetime values determined (including the influence of front/back recombination, etc.) are closely related to the open circuit voltage which is a macroscopic parameter that might be affected by any carrier lifetime non-uniformity. Therefore, information about the influence of spatial inhomogeneities on the carrier transport is important to assess whether it is enough to use local parameters to correlate different characterization results —and to predict the performance of the solar cell—, or to what extent it is required to consider non-uniform parameters that could be more representative of the whole device.

In this contribution, we use transient PL measurements spatially resolved in the micrometer-scale range to access the carrier properties of different absorbers. The TRPL setup is coupled into a microscope enabling to operate in confocal or widefield illumination mode. Widefield mode is used to map the samples in a broader range while confocal mode attempts to resolve the influence of the grains inside the structure with the highest optical resolution of the system (< 1 µm). Besides all the mechanisms involved in the determination of the effective carrier lifetime such as surface recombination, charge separation, etc., the use of confocal mode requires the consideration of lateral diffusion of carriers as well as the proper evaluation of the sample performance due to possible high injection effects. Accordingly, the interpretation of the measurements in both modes is aided by 2D simulations, which are also based on the macroscopic I-V parameters of the devices. Specifically, 2D device simulations allow us to quantify the lateral diffusion of carriers as well as to include other key parameters involved in TRPL measurements, i.e. surface recombination or carrier mobility. All simulations use as input measured absorption coefficient as a function of the bandgap grading for improved modelling. Finally, results from other spatially resolved techniques will be shown to correlate device performance with TRPL mapping and support the main findings.

Numerical simulations of solar cell device physics for predicting the performance, design and optimization of solar cells is a well explored active area of research. There are many tools and software packages like AFORS-HET, SCAPS-1D, AMPS-1D, PC1D, Silvaco TCAD, Sentaurus TCAD, etc., which are available freely or commercially, to perform numerical simulation of solar cells. The fundamental physics equations solved are continuity equations for charge carriers, namely electrons and holes, and the Poisson equation for electrostatic potential. In the continuity equation for electrons and holes the generation and recombination term is modeled through radiative processes, the SRH process, the Auger process etc. For the SRH generation recombination process an effective lifetime is assumed in the modeling. Combining this model with the boundary conditions, light and temperature simulation conditions, one can calculate I-V curves, efficiencies, fill factors etc., for the solar cell. As the solar cell ages performance is affected. This can be microscopically explained through the transport of different defects present in the solar cell. The transport of defects can also cause metastability in solar cells. In our previous work we explained the metastable behavior of CdTe solar cells by studying the Cu related defect transport along with the carrier transport.

In this work, we present a novel Unified Solver for studying carrier and defect transport on an equal footing. The generation recombination term in the continuity equation for defects corresponds to the formation and transformation of defects. This formation and transformation of defects along with generation and recombination process for charge carriers is represented as a defect chemical reaction. Hence, we call our model as reaction-drift-diffusion modeling of solar cell. The drift-diffusion equations for defects require the diffusion constants and activation energies of the defect to be known and the defect chemical reaction require reaction rate constants to be known. These parameters are calculated using Density Functional Theory (DFT).

Since the main goal of our research work is to study short time metastability and long-time reliability concerns of cadmium telluride (CdTe) photovoltaics, special attention has been placed in the design of the solver to be able to produce results ranging from ns to hours/days/years. The solver gives us possibilities to explicitly account for all transient effects with free carriers (simulation of time resolved photoluminescence) and defects (simulation of performance instabilities, IV hysteresis etc). Various generation recombination processes can be represented as additional defect chemical reactions. Moreover, the Unified Solver supports accurate treatment of interfaces and grain boundaries that are crucial for the explanation of the operation of CdTe and other chalcogenide PV technologies.

The Unified Solver is benchmarked against Silvaco simulation in homojunction and heterojunction solar cell. Excellent agreement is observed between the Unified Solver and Silvaco results for the key solar-cell parameters (short-circuit current and open-circuit voltage). Next, the Unified Solver is employed in constant temperature 2D simulation of chlorine diffusion annealing in a cadmium telluride (CdTe) system under insulating boundary conditions (isolated system). Chlorine is introduced in the system as a neutral interstitial at a half corner of the (1nm×1.2nm) structure. The concentration of chlorine interstitial is 1e16 cm⁻³ and the system is kept at a temperature of 750K. The sample is annealed for 240s using the test case of chlorine defect reactions. The time evolution of chlorine substitutional defect (Cl⁺) is presented. Emulation of process temperature profiles is also presented in the talk.
For solar technology to compete with traditional energy sources, a continued decrease in photovoltaic (PV) energy generation cost is needed. Next-generation PV technology can achieve this by utilizing earth-abundant materials and low-cost processing techniques. Chalcogenide compounds are of particular interest in this area due to their prolific use in energy applications and amenability to high-throughput, low-cost processing techniques. Chalcogenides semiconductors have shown particular success in PV applications with materials such as Cu(In,Ga)(S,Se)$_2$ (CIGS), Cu$_2$ZnSn(S,Se)$_4$ (CZTS), and CdTe. However, developing new materials and processing techniques require extensive research efforts to achieve the required high-performance goals. Complex device processing and non-ideal optoelectronic properties associated with early stage materials often prolong material development.

In this work, our approach to developing next-generation semiconductors for PV is shown. We utilize low-cost, scalable solution-based processing techniques which are amenable to high-throughput optimization and a variety of chalcogenide precursors. Furthermore, we utilize advanced optoelectronic and structural characterization to guide the material development process; this provides rapid feedback for accelerated material development through accurate screening of early-stage materials for relevant optoelectronic properties and optimal synthesis parameters. In particular, we focus on the extraction of optoelectronic properties relevant for device performance – without the need for device fabrication – through optical techniques. Previous work using these techniques for developing CZTS, CIGS, and perovskites will be shown, with application to new materials currently in development. Ultimately, the successful development of new semiconductor materials requires a cross-disciplinary approach linking fundamental material properties and processing to the device-relevant optoelectronic properties.

2:00 PM ES20.02.02


Sb$_2$(Se$_3$) is becoming a relevant thin film chalcogenide semiconductor with different technological applications such as: superconductivity, electronic components, electrode for sodium-ion batteries, photodetectors and as emerging photovoltaic absorber. In particular, and for this last application, the material has shown remarkable improvements in the last few years, demonstrating solar cells in substrate configuration with different conversion efficiencies reaching 7.6%. In fact, and similarly to CdTe, most of the devices reported in the literature so far have been prepared using this configuration. This has opened interesting perspectives for their use in solar energy conversion applications, also taking into account the 1D crystalline organization of the material, with in principle benign grain boundaries and anisotropic conduction properties. Additionally Sb$_2$(Se$_3$) has shown a high flexibility degree in terms of substrate type, due to the relatively low synthesis temperatures required for optimal high quality polycrystalline growth (300-400 C), allowing deposition onto polymeric, steel, ceramic and TCO/glass substrates. This versatility makes this compound very promising for ubiquitous applications such as building integrated photovoltaics (BIPV) (flexible, bifacial, and semi-transparent), wearables, or autonomous IOT applications among others.

In this work we present a systematic optimization study of the synthesis of Sb$_2$Se$_3$ thin films using substrate configuration solar cells, by a sequential process based on reactive annealing under Se atmosphere of thermally evaporated Sb$_2$ layer precursors. The study is centered in the analysis of the Sb precursor thickness and reactive thermal annealing conditions (annealing temperature, time, and pressure) on the compositional, structural and morphological properties of the layers. We observe the formation of continuous layers with large and homogeneous crystals, reporting for first time a weak photoluminescence signal close to 1.3eV in agreement with the band gap value obtained by IQE, and a systematic vibrational characterization under resonant and non-resonant Raman conditions that allows report 15 peaks of the expected order. After a first optimization on Mo coated soda lime glass substrates, we report a promising power conversion efficiency of 5.3% in substrate configuration with a Voc of 403 mV (the highest value reported for this configuration to the best of our knowledge), close to the 7.6% certified world record in superstrate one.

Additionally the study is complemented with a wide characterization of the fundamental properties of Sb$_2$Se$_3$ layers and devices using morphological and physical-chemical characterization (Photoluminescence, SEM, XRF, XRD), and with a complete analysis of the impact of the absorber stoichiometry under different regimes (Se-rich, Se-poor, Sb-rich and Sb-poor conditions). This will be correlated with the optoelectronic characterization (JV, IQE, CV) of the solar cells. Finally, the main challenges to develop Sb$_2$Se$_3$ type solar cells in substrate configuration will be reviewed in the frame of the obtained results.

2:15 PM ES20.02.03

Antimony Chalcogenide with Tunable One-Dimensional Ribbons Thin-Film Solar Cells Grown by Close-Space Sublimation Liping Guo, Baiyu Zhang, Lin Li, Xiaofeng Qian, and Feng Yan; 1The University of Alabama, Tuscaloosa, Alabama, United States; 2Texas A&M University, College station, Texas, United States. 3IREC, Barcelona, Spain; 3IN2UB, Departament d'Electrònica, Universitat de Barcelona, Barcelona, Spain.

The non-cubic antimony chalcogenides, i.e., Sb$_2$Se$_3$, formed by quasi-one-dimensional ribbons can enhance light absorption and carrier transport by tuning the ribbon direction using the close-space sublimation (CSS) deposition. The power conversion efficiency (PCE) ~7% is found to be associated with the ribbon direction, which was investigated with theoretical calculation and experimental measurement in the Sb$_2$Se$_3$ films and devices. The substrate temperature and film thickness are critical for the fine-tuning of ribbon orientations during the CSS deposition. Our results show that [211] preferred orientation leads to the minimum series resistance and highest light absorbance in the device. The device reliability measurement and in-depth elemental profiling analysis suggest that the interdiffusion between window layer and absorber layer dominate the degradation mechanism. This observation demonstrates that Sb$_2$Se$_3$-like quasi-one-dimensional profilings with van der Waals boundaries can achieve scalable production at low cost and hold great potential for next-generation solar cell.

2:30 PM ES20.02.04

Recent Advances in Si/CIGS Tandem Cells Daniel Lincoat; CNRS-IPVF, Palaiseau, France.

Tandem cells are considered as the next generation solar cell to overpass the intrinsic efficiency limitations of single junction solar cells, fixed by the Shockley Queisser limit below 33% and more probably below 30%. Silicon solar cells are already approaching the theoretical limit of about 29%, and represent 95% of the present PV Market. Tandem solar cells on silicon would make possible to reach 43% theoretical limit, making practical module efficiencies of more than 30%. Combinations with hybrid perovskite and III-V top cells are presently focusing a lot of attention, but an alternative is to develop top cells based on chalcogenide materials, which technologies are well proved on the market (CdTe and CIGS). This presentations will review on researches carried out on silicon/CIGS solar cells. Based on the experience on single junction CIGS low band solar cells (1.15 eV) at about 20% efficiency, wide gap CIGS solar cells (1.6-1.8 eV) are grown on single crystal silicon substrates by coevaporation, with lattice parameters matching with silicon, thanks to compositional adjustments (Ga to In, S to Se). In order to give more flexibility in interface electrical engineering, the silicon substrate is functionalized by a thin III-V buffer layer, based on GaAlAsP lattice matched alloys. Epitaxial growth of CIGS has been successfully demonstrated and first devices have been elaborated for the formation of high efficiency top cells alone, using Si/III-V as a selective back contact. Further structural, chemical and luminescence characterization will be reported.

Ref: 1D. Lincoat et al., Proceedings of EUPVSEC 2018

3:00 PM BREAK

3:30 PM ES20.02.05


A large gap still remains between the achieved conversion efficiencies and the Shockley-Queisser limit for Cu(In,Ga)Se$_2$ (CIGS) based solar cells. Some of the current limitations such as parasitic absorption losses are known and solutions are being developed. For some other limitations the origin is not well understood yet, but is required for knowledge based improvements. Thorough materials and device characterization of highly efficient solar cells can help to understand the origins of the remaining losses. We used advanced materials and device characterization including high resolution transmission electron microscopy, time-of-flight secondary ion mass spectrometry, and time resolved photoluminescence (TRPL) combined with multidimensional device modelling to confine the origins of the remaining losses. We will summarize our recent findings on...
optical, compositional, structural and electronic properties in multi-stage co-evaporated CIGS layers and at interfaces to adjacent layers. In particular, we will describe how surface recombinations velocities, minority carrier lifetime and mobility can be extracted from TRPL measurements and what we can learn from these findings. Further, we will present the presence of undesired compositional non-uniformities & voids and discuss their formation mechanism and role on device performance. Combined with recent findings obtained on narrow band gap CIS absorbers our results indicate possible inherent limitations originating from current fabrication methods and device architecture, which leads to new strategies how the actual CIGS solar cell efficiency can be pushed closer to the Shockley-Queisser value.

4:00 PM ES20.02.06
12.2% CIS and 13.6% CIGS Solar Cells Fabricated from Copper-Rich DMF Molecular Precursor Solutions Jingjing Jiang, Shaotang Yu, Sanping Wu, Weibo Yan and Hao Xin; College of Materials Science and Engineering, Nanjing University of Posts & Telecommunications, Nanjing, China.

Recently, 22.8% efficient Cu(In,Ga)Se₂ (CIGS) thin film solar cell has been reported, demonstrating its great potential as a competitor to silicon solar cells. Adopting solution method to prepare highly efficient CIGS light absorption materials is crucial for reducing the cost of CIGS solar cell fabrication and achieving large-scale production. We have previously reported 10.3% copper indium selenide (CIS) solar cell with the absorber fabricated from single DMF molecular precursor solution, demonstrating the great potential of DMF as environmentally benign solvent for solution processed thin film solar cells. The metallic element ratio (Cu/In or Cu/(In+Ga)) is the key factor to affect the quality of absorber materials. Here, we have systematically investigated the effect of the Cu/In ratio (0.85 to 1.2, from Cu-poor to Cu-rich) in the precursor solution on the CIS device performance. We found that solar cell efficiency increases with the Cu/In ratio from 0.85 to 1.05 and then decreases from 1.05 to 1.2. The best device was achieved from a ratio of 1.05 with a peak power conversion efficiency (PCE) of 12.20%, a short circuit current density (Jsc) of 36.12 mA/cm², an open circuit voltage (Voc) of 0.499 V, and a fill factor (FF) of 67.57%. Further, by gallium alloying, CIGS solar cell with a PCE of 13.6% has been fabricated with a Voc of 0.600 V, Jsc of 34.78 mA/cm² and FF of 65.17% under similar Cu-rich (Cu/(In+Ga)=1.05, Ga/(In+Ga)=0.2) condition. Our results for the first time demonstrate highly efficient CIS/CIGS solar cells can be achieved from absorbers grown under Cu-rich conditions. Characterization of the absorber materials and solar cell devices are undergoing to understand the mechanism behind the phenomenon observed.

4:15 PM ES20.02.07
Wet-Chemical Treatment of Cadmium Telluride (CdTe) Photovoltaics for Enhanced Open-Circuit Voltage (Voc) and Fill Factor (FF) Ebin Bastola and Randy J. Ellingson; University of Toledo, Toledo, Ohio, United States.

Cadmium telluride (CdTe) thin film solar cells are renowned photovoltaic materials for its high absorption coefficient, suitable band gap and low manufacturing cost. The fabrication of highly efficient devices has achieved reduced intrinsic defects and improved interfaces at front and back contacts. The back-contact processing includes the formation or deposition of tellurium (Te) layer to make an ohmic contact with a metal. Here, we report wet-chemical treatments of CdTe using various iodine compounds and sodium tetrafluoroborate (NaBF₄). The iodine compounds tested are elemental iodine (I₂), ammonium iodide (NH₄I), mixture of iodine and ammonium iodide (I/F₄) and formamide iodide (FAI). The treated surfaces were studied using Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The treatment with iodine compounds produced Te rich layer on the back surface based on Raman, XRD patterns and changed surface morphology. The fabrication of the devices after these treatments, except 1-propanol, improved the open-circuit voltage (Voc) and fill factor (FF) of the devices. The 1-propanol etching produced tellurium iodide (TeI) in β-phase on the surface which reduced device performance. The photocurrent conversion efficiency of CdTe devices after treatment is up to 14.0% (Voc= 841 mV and FF 78%) while untreated devices have an efficiency of about 12.7% (Voc= 814 mV and FF 73%). In case of BF₄⁻ treated samples, it did not produce Te rich layer, but it seems BF₄⁻ ions are passivating CdTe surface with enhanced Voc and FF compared to standard devices.

4:30 PM +ES20.02.08
Status and Challenges of CdTe Photovoltaics Wyatt Metzger; National Renewable Energy Laboratory, Golden, Colorado, United States.

CdTe solar technology is producing electricity at costs less than conventional fuels in many regions. Yet despite its commercial maturity, there is still headroom to increase performance significantly by addressing fundamental material challenges including compensation, hole density, carrier lifetime, and interfaces. This presentation will describe ongoing work to understand and overcome these challenges.

SESSION ES20.03: Poster Session I: Material Growth

Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

ES20.03.01
Revealing the Optimal Conditions for the Synthesis of High Efficiency Cu₂ZnSnGe₂ Wide Band Gap Absorber Nada Benhaddou 1, Meco Lamo Molanda 1, Zakaria Laghourami 2 and Zouheir Sekkat 3; 1IRCAM, Barcelona, Spain; 2Optics & Photonics Centre, Moroccan Foundation for Advanced Science & Innovation & Research, MASCIR, OCP Foundation, Rabat, Morocco; 3Department of Chemistry, Faculty of Sciences, Mohammed V University in Rabat, Rabat, Morocco.

Last advances on kesterite (Cu₂ZnSn(S,Se)₄) corroborate the importance of doping and alloying strategies, not only for tuning the properties of this family of materials, but also for achieving higher efficiencies and broadening their possible range of application. Alkaline (Li, Na, K) and Ge doping; as well as Ag, Cd and Ge alloying are demonstrating a high potential by enhancing different aspects of these materials. Here, we have systematically investigated the effect of the Cu/In ratio (0.85 to 1.2, from Cu-poor to Cu-rich) in the precursor solution on the CIS device performance. We found that solar cell efficiency increases with the Cu/In ratio from 0.85 to 1.05 and then decreases from 1.05 to 1.2. The best device was achieved from a ratio of 1.05 with a peak power conversion efficiency (PCE) of 12.20%, a short circuit current density (Jsc) of 36.12 mA/cm², an open circuit voltage (Voc) of 0.499 V, and a fill factor (FF) of 67.57%. Further, by gallium alloying, CIGS solar cell with a PCE of 13.6% has been fabricated with a Voc of 0.600 V, Jsc of 34.78 mA/cm² and FF of 65.17% under similar Cu-rich (Cu/(In+Ga)=1.05, Ga/(In+Ga)=0.2) condition. Our results for the first time demonstrate highly efficient CIS/CIGS solar cells can be achieved from absorbers grown under Cu-rich conditions. Characterization of the absorber materials and solar cell devices are undergoing to understand the mechanism behind the phenomenon observed.

For this purpose, Cu₂ZnGeSe₂ thin films were synthesized onto Glass/Mo substrates by a sequential process, based on the sputtering of Cu, Zn and Ge metallic layers, followed by a reactive annealing under a Se₂/Ge atmosphere inside a graphite box. Parameters like metallic stack order; annealing temperature (450-550 °C), pressure (1-1000 mbar), routine (one or two-step annealing) and time; as well as the composition and of the use of chemical etchings were investigated. Additionally, a combinatorial sample with compositional gradients was prepared covering the full Cu/Zn, Cu/Ge and Zn/Ge range of interest, in order to correlate composition with the formation of secondary phases and defects. All the samples were fully characterized using a complete set of techniques (XRF, Raman spectroscopy, XRD, SEM and EDX) and by preparing and measuring solar cell devices. After trying several stack orders, Cu/Ge/Zn/Ge is selected as the most promising one, leading to the formation of less secondary phases. The optimization of the annealing parameters confirms that a two stage process is the best strategy for obtaining high quality absorbers. This includes a stage at relatively low temperature (330 °C) for the synthesis of the CZGSe compound, and a second step at relatively high temperature (480 °C) for its crystallization, revealing that lower annealing temperatures than in the case of the pure Sn compound are required. The compositionally graded sample shows that best efficiencies are obtained for absorbers with Cu/Ge ratio around 0.67 and Zn/Ge around 1.10, suggesting that Cu and Zn-poorer conditions than for pure Sn kesterite are required. Using this compositionally graded sample, we will present a deep analysis of the correlation of the different optical, electrical parameters with composition, including the analysis of secondary phase and possible point defects formation. We will highlight the importance of the Cu/Ge ratio which includes an etching of the absorbers in KCN, a champion cell with an efficiency of 6.5% (Voc = 556 mV, FF = 59.6%, Jsc = 19.6 mA/cm²) is reported. Additional experiments introducing different sources of Ge during the annealing process (GeSe, GeS, and pure Germanium) in order to change the partial pressure inside the graphite box will also be presented.

ES20.03.02
Beyond 13% Efficient CuSbS₂ Films Exhibited Optical Absorption Coefficients Higher than 10^4 cm⁻¹ after Heating. The optical band gap of the as-deposited films was of 1.6 eV, which decreased to 1.46 and 1.24 eV after heating the films at 300 and 500 °C, respectively. All the deposition parameters were kept constant: temperatures, from 300 to 500 °C, to make them crystalline and form the ternary compounds. The results showed that the film thickness depends on the sulfur load, deposition time, and temperatures.

Researchers have developed either transition metals-doped SnS films or the synthesis of novel semiconductor ternary materials based in Sn and S such as Sn-Sb-S (TAS): SnSb₂, SnSb₃₄, and Sn₃Sb₃₄. Conventionally, ternary compounds are synthesized by deposition of individual intercalated layers of SnS and SbS₃, followed by annealing at high temperatures.

In this work, SnS and SbS₃ thin films have been obtained by in-situ chemical bath deposition. The effect of the sulfur load, time deposition and pH bath solution has been studied. Antimony and tin chloride were used as metal ion sources, thioacetamide as sulfur ion source, and tartaric as the complexing agent. Chemical bath deposition was carried out at 80°C varying the concentration of sulfur and time of deposition while the pH of the solution was kept between 8 and 9. Then, the resulting samples were heated in nitrogen at temperatures from 300 to 500 °C to make them crystalline and form the ternary compounds. The results showed that the film thickness depends on the sulfur load, deposition time, pH and the temperature during the heating. The thickness of the as-deposited film without excess of sulfur was of 117 nm for a time deposition of 2 h. An increase on the sulfur load produced thicker films with thickness above of 250 nm. The SEM image of the as-deposited films showed a morphology of elongated grains of 100 nm, which increase their size after heating. The optical band gap of the as-deposited films was of 1.6 eV, which decreased to 1.46 and 1.24 eV after heating the films at 300 and 500 °C, respectively. All the TAS films exhibited optical absorption coefficients higher than 10^4 cm⁻¹. Moreover, the photo-conductivity of the as-deposited films was of 10^7 Ω⁻¹ cm⁻¹ while those heated at 300 and 500 °C showed photo-conductivities of 10^4 to 10^7 Ω⁻¹ cm⁻¹. Finally, the evaluation of these ternary absorbers into the FTO/CdS/TAS/C structure gave a Voc of 462 mV and a Jsc of 2.37 mA/cm² under white-LED light. These preliminary results showed that TAS absorbers could be good candidates to obtain higher Voc values than those obtained with the SnS-based SCs.

Beyond 13% Efficient CuZnSn(S,Se)₂ Solar Cells from DMSO Molecular Precursor Solution Yunchai Gong, Yifan Zhang, Weibo Yan and Hao Xin; Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (JINAM), Nanjing University of Posts & Telecommunications, Nanjing, China.

Kesterite CuZnSn(S,Se)₂ (CZTSSe) semiconductors, composed of non-toxic and earth-abundant elements, have great potential as low cost and mass production photovoltaic absorber materials. However, the best CZTSSe solar cell, obtained from hydrazine based ink by IBM in 2014, only has an efficiency of 12.6% [1], much lower than similar structured Cu(In,Ga)Se₂ (CIGS) solar cell (22.6% [2]). The development of kesterite CuZnSn(S,Se)₂ thin-film solar cells is currently hindered by the large open-circuit voltage deficit (Voc-oc). The possible reasons for the large Voc-oc include large tail states (electrostatic potential fluctuation and bandgap fluctuation), Cu-Zn antisite order-disorder, formation of deep defects and interface formation, which is dominate still under debating. Here, we have explored different strategies to understand the Voc deficit in DMSO solution processed CZTSSe solar cells. First, we found that the Voc-oc as well as efficiency of DMSO solution processed CZTSSe solar cells is strongly affected by the pressure and temperature of DMSO solution (Sn²⁺:Sn³⁺) in the solution. The power conversion efficiency achieved from Sn²⁺ solution was 13.2% with a Voc-oc of only 0.570 V, much lower than the current world record CZTSSe device (0.617 V), whereas the efficiency obtained from Sn³⁺ solution was only 7% with Voc-oc higher than 0.680 V. Investigation by solution chemistry and film morphology characterization reveals that the huge difference comes from different complexation of the Sn with ligand (thiourea) and solvent (DMSO) which lead to different reaction pathways from solution to solid state film and thus dramatic absorber quality and device performance. Second, we have used Ag or Ge alloying to further investigate the effects on the Voc-oc of Sn²⁺ solution processed CZTSSe solar cells. Characterization of CZTSSe absorber materials including XRD, Raman, SEM, EDX, TEM, and PL and device performance show positive effect of the alloying on Voc-oc issue. Our results shed new light on how to suppress CZTSSe solar cell Voc-oc and improve their efficiency to higher level.


Crystalline antimony-based nitrides have long posed fabrication challenges due to the high nitrogen chemical potential required for formation and the tendency of antimony to react with oxygen and moisture to form amorphous oxynitrides. To date, Zn₂SnN₂ is the only reported crystalline antimony nitride in which Sn functions as a cation with a positive oxidation state. This material warrants further investigation not only due to its unique nature, but also due to its advantageous optoelectronic properties, which may be tunable like those of other ternary nitrides. Theoretical calculations predict this material to have a direct band gap of 5.9 eV, which suggests that Zn₂SnN₂ has promise as a photoactive absorber. [1] Experimental measurements show room-temperature photoluminescence and band edge alignment appropriate for the hydrogen evolution reaction.

In this work we report on the detailed investigation of the optoelectronic properties of thin-film Zn₂SnN₂ and their correlation to the films’ composition. Films were grown through combinatorial co-sputtering and characterized by spatially-resolved measurements. Experimental results show that the wurtzite-derived crystal structure is stable over a large range of composition (Zn/Zn₂Sn₂N₂ = 60-80%) as determined by X-ray fluorescence. 4-point-probe measurements reveal 200-400 KΩm resistance, tunable with composition. UV-visible spectroscopy shows an absorption onset around 1.7 eV. This will be further investigated through photoluminescence and Hall effect measurements. Growth parameter space will be mapped by varying factors such as growth rate, substrate temperature, and the use of a N₂-cracker to enhance the nitrogen chemical potential. A fuller understanding of the relationship between fabrication conditions and film properties will help evaluate the attainability of this new ternary nitride’s predicted utility as a photovoltaic material.


CZTS Solar Cells Absorbers Produced by Sputtering or Pulsed Laser Deposition Jorgen Schou1, Mungunshagai Gansukh2, Filipe Martinho3, Simon Lopez-Martino4, Moises Espindola-Rodriguez2, Alireza Hajijafarassar5, Eugen Stamatie6, Sara Engelberg1, Andrea Crovetto1, Stela Cataneescu2 and Ole Hansen3; 1TU Denmark, Roskilde, Denmark; 2DTU Fotonik, TU Denmark, Roskilde, Denmark; 3DTU Nanotech, TU Denmark, Kgs. Lyngby, Denmark.

Currently CZTS sulfide absorbers for solar cells with the highest efficiency have all been produced by vacuum techniques which thus seem to be superior to solution processing for CZTS cells. Sputtering and pulsed laser deposition are typical vacuum deposition techniques, which are employed for solar cell absorbers of complicated stoichiometry. Both techniques are well-known for stoichiometric transfer of chemical compounds such as metal oxides and nitrides from a target to a substrate. The two techniques are non-thermal since the emitted atoms from the target are quite energetic and may have an energy distribution with a tail up to more than 10 eV. This non-thermal arrival energy is also known to be beneficial for growth of layers with high crystallinity.

In the photovoltaic literature there seems to be a limited number of examples of a comparison between the absorbers and cells produced by either sputtering deposition (SD) or pulsed laser deposition (PLD) except for an inconclusive study without production of solar cells by Sun et al. [1].

We have recently produced solar cells by co-sputtering deposition and PLD with a record efficiency of 6.6 % for SD, while that by PLD reached 5.2 % [2]. While the efficiency was comparable, there were several processing differences, in particular in the thermal annealing steps. It is not clear how different the ideal thermal profiles for the two techniques are.

In the photovoltaic literature there seems to be a limited number of examples of a comparison between the absorbers and cells produced by either sputtering deposition (SD) or pulsed laser deposition (PLD) except for an inconclusive study without production of solar cells by Sun et al. [1].

We will discuss a few other PLD experiments: The CZTS-films can be doped with additional elements, e.g. by Ag using doped targets without any additional complications in the PLD process. Also the production of oxide precursor films is comparatively easy with an oxide target for PLD, while it is not yet clear how successful a detour via metal oxides to
sulfides would be for co-SD.

Detailed results for the comparison between films made by SD and PLD as well as examples PLD-films of other compositions will be shown in this contribution.


ES20.03.06 Engineering Ga Profile in Low Temperature-Processed Cu(In,Ga)Se₂ Thin Film by Using a Thin Ag Precursor Layer Jong-keuk Park

Low-temperature-processed Cu(In,Ga)Se₂ (CIGS) thin film absorber is important for demonstrating a functional CIGS solar cell on plastic substrates. However, control of the band profile mainly dominated by the Ga concentration profile in the CIGS film has been challenging due to slow atomic diffusion at low temperatures. Here, a systematic engineering of Ga profile in CIGS films is reported by employing a thin Ag precursor layer prior to CIGS co-evaporation. By increasing the Ag precursor layer thickness, Ga gradient was mitigated along with improved CIGS grain size, which enhanced overall solar cell performance. Formation of liquid-phase Ag-Se could provide mobile channels for Ga diffusion along the grain boundaries and expedite CIGS recrystallization process at such a low temperature.

ES20.03.07 Enhanced Optical and Electronic Properties of 2D n-MoS₂ by Thin-Layer Al₂O₃ Surface Passivation for Photovoltaic Applications Atteq U. Rehman and Soo H. Lee

Transition Metal Di-Chalcogenides (TMDs) have shown a great promise for being used as a 2D layered semiconductor materials and offers excellent photon absorption and electronic transport properties for photovoltaic applications. Among these TMDs, layered molybdenum disulfide (MoS₂) is one of the most promising candidate for ultrathin-film solar cell fabrication with excellent performance, superior flexibility and lower costs. An n-type bulk like MoS₂ deposited on p-Si, establishes a built in potential at n-MoS₂/p-Si interface that governs the carrier separation for photovoltaic operation. We present an aluminum oxide (Al₂O₃) based surface passivation on multilayered n-MoS₂/p-Si solar with enhanced photoelectric properties. This improved performance is due to the fact that Al₂O₃ helps in reducing the interface trap density at the MoS₂ surface and performs n-type field effect passivation by fixed charges present in Al₂O₃ layer. By adding Al₂O₃ based MoS₂ surface passivation to our device an improved power conversion efficiency (PCE) of 5.6% with enhancement in Jₚ, Voc, and FF was observed. In addition to improvement at MoS₂ surface by passivation and superior Jsc, Al₂O₃ effectively enhanced the built-in potential at n-MoS₂/p-Si junction, that help to promote the e⁻ – h⁺ pairs separation. Our work demonstrates the integration and effectiveness of the surface passivation for the bulk-like MoS₂ films with Si-based electronics to develop highly efficient photovoltaic cells.

ES20.03.08 Solution-Processed Earth-Abundant Cu₄BaSn(S₅Se₅)₂ Solar Absorber Using a Non-Toxic Solvent Beentu Teymur, Yihao Zhou, Edgard Ngaboyamahina, Jeffrey T. Glass, and David B. Mitzi

Optically transparent p-type conductors enable development of transparent electronics, and opportunities to develop high-efficiency bifacial photovoltaic devices. Sulfide materials offer an interesting alternative to oxides for the photovoltaic applications due to better hole transport properties. We report on the structural, optical, and electronic properties of earth-abundant p-type transparent conducting barium copper sulfide (BCS) thin films fabricated using solution-processing. The BCS thin films were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–Vis–NIR spectroscopy, and spectroscopic ellipsometry (SE). A BCS film of thickness 100 nm can transmit > 70% of the visible light with band gap ~ 2.4 eV. Based on SEM images, initial BCS films look compact with a grain size of ~15 nm. Our studies show that these films are conductive with a carrier concentration of ~10¹⁷ cm⁻³, making them promising hole transport materials for photovoltaic applications. We will discuss cadmium telluride (CdTe) devices fabricated using BCS layer as an interfacial layer between CdTe and a standard Cu/Au. Additionally, we will extend our study to fabricate bifacial CdTe devices employing the transparent BCS buffer layer and a conducting oxide as the back contact.

ES20.03.09 Chemical, Structural and Photovoltaic Properties of Cd Chalcogenide Thin Films Grown by Chemical Bath Deposition on GaAs(100) Ollir Friedman, Omri Moschovitz and Yuval Golan

Cd chalcogenide films are direct band gap semiconductors that can harvest photon energy in a wide energy range from 2.42 eV (CdS) to 1.74 eV (CdSe) by compositional tuning or chemical gradient. Growth of such films using chemical bath deposition is advantageous due to low production costs and the ability to easily control bath composition and resulting film microstructure. We have recently demonstrated monocrystalline CdS and CdSe deposited on GaAs substrates by chemical bath deposition.1,2 In this work we present the chemical, structural and photovoltaic properties of Cd(S,Se) solid solution thin films.3 We present evidence for the formation of chemically graded films which can be expected since thiourea (S precursor) decomposes faster than sodium selenosulfate (Se precursor) and as a result, S anions are first to react with the substrate surface. The physical and chemical properties of the films were characterized using x-ray powder diffraction, scanning electron microscopy, analytical transmission electron microscopy and energy dispersive spectroscopy mapping. Finally, current-voltage measurements of a GaIn-eutectic/GaAs/Cd(S,Se)/In device were conducted at room temperature under 1 sun. We demonstrate increasing photo-response with S/Se ratio in CdS,Se₁₋ₓ based photovoltaic cells. This work presents a comprehensive and applicable study on chemical bath deposited Cd chalcogenide thin films.


ES20.03.10 Semi-Transparent P-Type Barium Copper Sulfide as an Interface Layer for Cadmium Telluride Solar Cells Kamala Khanal Subedi, Ebin Bastola, Indra Subedi, Nikolai Podrza and Randy J. Ellingson; The University of Toledo, Toledo, Ohio, United States.

Optically transparent p-type conductors enable development of transparent electronics, and opportunities to develop high-efficiency bifacial photovoltaic devices. Sulfide materials offer an interesting alternative to oxides for the photovoltaic applications due to better hole transport properties. We report on the structural, optical, and electronic properties of earth-abundant p-type transparent conducting barium copper sulfide (BCS) thin films fabricated using solution-processing. The BCS thin films were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–Vis–NIR spectroscopy, and spectroscopic ellipsometry (SE). A BCS film of thickness 100 nm can transmit > 70% of the visible light with band gap ~ 2.4 eV. Based on SEM images, initial BCS films look compact with a grain size of ~15 nm. Our studies show that these films are conductive with a carrier concentration of ~10¹⁷ cm⁻³, making them promising hole transport materials for photovoltaic applications. We will discuss cadmium telluride (CdTe) devices fabricated using BCS layer as an interfacial layer between CdTe and a standard Cu/Au. Additionally, we will extend our study to fabricate bifacial CdTe devices employing the transparent BCS buffer layer and a conducting oxide as the back contact.
ES20.03.11
Deposition of Cd$_{1-x}$Zn$_x$Se$_{1-y}$Te$_y$ by Closed-Space Co-Sublimation for Wide-Bandgap Top Absorbers in Tandem Photovoltaic Devices
Cayre Reich$, Arthur Onno$,
Joe Carpenter*, Tushar Shimp†, Amit Munshi†, Andrew Ferguson‡, Wyatt Metzer‡, Walajabab Sampath* and Zachary Holman$; Colorado State University, Fort Collins, Colorado, United States; *Arizona State University, Tempe, Arizona, United States; National Renewable Energy Laboratory, Golden, Colorado, United States.

Wide bandgap Cd$_{1-x}$Zn$_x$Te (CZT) is of interest for a top cell in tandem devices because it has a tunable bandgap and is expected to leverage the low cost CdTe fabrication process. However, the vapor pressure of CdCl$_2$ is orders of magnitude higher than that of CdTe; at activation temperatures, which results in Zn loss during processing, thereby reducing the bandgap. In the CZT films, the Zn can be replaced with the Cd of the CdCl$_2$ treatment or simply leave Zn vacancies in the film. Either of these effects are detrimental to device performance and make it challenging to fabricate higher bandgap absorbers based on CdTe. Here, we investigate CZT composition for films activated in an enclosed box with varying CdCl$_2$ and ZnCl$_2$ vapor pressures. We will determine how controlling the vapor pressure of the two Cl sources affects the evolution of the CZT film. These results will allow us to determine if Zn loss can be avoided.

ES20.03.12
Efficiency Improvement of Cu$_2$ZnSnS$_3$, Solar Cell by Optimizing the Interface Chemistry
Kaiwen Sun, Chang Yan, Jialiang Huang and Xiaoqing Hao; University of New South Wales, Kensington, New South Wales, Australia.

High bandgap kesterite Cu$_2$ZnSnS$_3$ (CZTS) has attracted world-wide attention in recent years owing to the earth-abundance and non-toxicity of its constituents and the realization of high and stable performance [1]. The large deployment of photovoltaic (PV) in the future would demand stable, abundant and non-toxic materials similar to Si, in either flexible/rigid single junction thin film solar cells or tandem cells with Si bottom cell. In this regards, CZTS is more advantageous over other single junction cells and their associated top cell for tandem cells. For its industrial-scale deployment, obtaining high efficiency CZTS is the first prerequisite. Until recently, however, state-of-the-art CZTS devices were limited under 10%, being far below the Schockley-Queisser (SQ) limit of about 33% efficiency under terrestrial conditions [2]. Major limitations lie in the large open circuit voltage deficit (Voc-deficit) and a comparably low fill factor (FF). The loss mechanisms for the Voc and FF have been extensively investigated and the hetero-junction interface quality is one of the most proposed factors that contribute to the performance limit. One of the critical elements of forming a desirable interface structure in hetero-junction PV technology is the junction-formation step [3]. At present, the preferred approach in CZTS community is to deposit a thin CdS layer by chemical bath deposition (CBD) method, where a suitable amount of ammonium hydroxide (ammonia) is applied as the complexing agent. The function of the ammonia has been extensively studied in CIGS (1) clean the absorber surface before the deposition, (2) control the cation slow release, (3) suppress the formation of detrimental impurity like Zn(OH)2 at the interface and (4) minimize the metastability behaviour of the device. In our successive ionic layer adsorption and reaction (SILAR) process for alternative ZnCdS buffer deposition, however, no ammonia has been applied. In order to further optimize the interface quality, we explored adding ammonia in the cation solution to realize its similar function in CdS deposition process. In summary, the CZTS/ZnCdS interface quality is optimized by applying ammonia as complexing agent in the precursor solution during the SILAR process for ZnCdS deposition. Excess oxide and hydroxide impurities formed at the interface are limited to a low level, which reduces the related electronic defects in the depletion region and alleviates the metastability behavior caused by the Zn(OH)$_2$. The application of ammonia also enables the control of reaction mechanism, improving the epitaxial growth, thereby reducing the interface recombination. Finally, efficiency of up to 10% is achieved by modifying the interface structure thanks to the chemical method.

ES20.03.13
Understanding and Controlling Zn Loss During CI Activation of Cd$_{1-x}$Zn$_x$Te Films
Adam Phillips, Fadhill K. Alfallahi, Geethika K. Liyanage, Bhujiyan Anwar, Manoj K. Jamarkattel, Jacob Gibbs and Michael Hebben; University of Toledo, Toledo, Ohio, United States.

Wide bandgap Cd$_{1-x}$Zn$_x$Te (CZT) is an attractive absorber material for thin film solar cells fabrication because it has a tunable bandgap and is expected to leverage the low cost CdTe fabrication process. However, the vapor pressure of CdCl$_2$ is orders of magnitude higher than that of CdTe; at activation temperatures, which results in Zn loss during processing, thereby reducing the bandgap. In the CZT films, the Zn can be replaced with the Cd of the CdCl$_2$ treatment or simply leave Zn vacancies in the film. Either of these effects are detrimental to device performance and make it challenging to fabricate higher bandgap absorbers based on CdTe. Hence, we deposited the quaternary alloy Cd$_{1-x}$Zn$_x$Se$_{1-y}$Te$_y$ using a modified close space sublimation (CSS) process from sources containing Cd$_x$Se$_{1-y}$Te$_y$ and Zn. The deposited films were characterized by Transmission and Scanning Electron Microscopy, Energy Dispersive X-Ray Spectroscopy, and X-ray Diffraction in order to assess their material properties and composition as a function of deposition parameters. Optoelectronic properties were assessed with Transmittance, Photoluminescence, and Time-Resolved Photoluminescence measurements. Preliminary device results will be reported.

ES20.03.14
Fabrication and Characterization of Selenized Stacked CISGe Absorber Layers by Evaporation Technique
Ganesh Regmi, J.S. Narro-Rios and S. Velumani; Sección de Electrónica del Estado Sólido (SEES), Departamento de Ingeniería Eléctrica, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional (CINVESTAV-IPN), Mexico City, Mexico.

Policrystalline CuIn$_{x}$Ga$_{1-x}$S$_3$ (CIGSe) quaternary semiconducting material is a mesmerizing absorber layer to fabricate the high-efficiency thin film photovoltaic device. Among the different evaporation growth processes of CIGSe thin film, the deposition of copper, Indium, Gallium, and selenium stacking layer structure is one of the versatile methods due to its simplicity, good stoichiometry, and resulting throughput efficiency in photovoltaic devices. In the experiment, the metallic elements copper (Cu), indium (In), and gallium (Ga) were deposited in specific orders at room temperature and then the whole structure was selenized at (450-550 °C) with different time of selenization (30-60 min). Selenization effect on structural, morphological, optical, and electrical properties of prepared films was studied. Results showed that the structural, morphological and optical properties of CIGSe thin films strongly depend on the growth mechanism, annealing temperature, time of selenization and chemical composition. X-ray diffraction (XRD) pattern showed the chalcopyrite structure of CIGSe with (112) preferred plane. The surface morphology and chemical composition of selenized thin films were investigated by scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The grains were transmuted from featureless melted to well faceted bladed tetragonal grains of CIGSe by SEM images. Raman spectroscopy exhibited A$_1$ mode peak along with B$_2$ mode peak. The root mean square (RMS) roughness of the films was studied by atomic force microscopy (AFM) and was ranged between 60 to 90 nm. The depth profile study showed that the distribution of elements depends upon the elemental order in the stacking structure. Optical testing was conducted by UV spectrophotometry and observed the absorption coefficient in the order of 10$^5$ cm$^{-1}$. The carrier concentration was varying from 10$^{10}$ to 10$^{17}$ cm$^{-3}$ by half effect Van der Pauw method. The results showed that 450 °C and 500 °C of selenization temperature was not sufficient for the inter-diffusion of all elements forming a good CIGSe absorber layer. Instead, the film selenized at 550 °C for 60 min showed a better result which could be a good absorber layer for highly efficient CIGSe based thin film solar cells.

ES20.03.15
XPS Analysis of the CuGaSe$_2$ - CuAlSe$_2$ Single Crystals Grown by CVT
dBarys Korzun*, Shanti Raykin†, Tai-De Li² and Jonathan Adam³; The City University of New York, Borough of Manhattan Community College, New York, New York, United States; ²Advanced Science Research Center at the Graduate Center of CUNY, New York, New York, United States.

Copper gallium diselenide (CuGaSe$_2$) and copper aluminum diselenide (CuAlSe$_2$) belong to the I-III-VI$_2$ group of compounds and are extensively studied as absorbing materials in solar cells and as active elements in optical filters. To optimize their properties, it is necessary to control their surface properties. The goal of the present paper is to investigate the effects of etching on the surface of the CuGaSe$_2$ – CuAlSe$_2$ single crystals and compare the results of chemical etching and argon ion beam sputtering.
Single crystals of seven alloys of the (CuGaSe)\textsubscript{x}(CuAlSe)\textsubscript{1-x} system, with \(x = 0.20, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90\), were grown by chemical vapor transport (CVT) in an evacuated quartz tube using iodine as a transporting agent. Typical dimensions of the grown plate-like single crystals were about 10 mm \(\times\) 5 mm \(\times\) 0.5 mm with a well-developed surface (112).

X-ray photoelectron spectroscopy (XPS) measurements were performed with PHI 5000 VersaProbe II XPS system using a monochromatic Al K\(\alpha\) source (15 kV). The pass energy was 117.4 eV for survey scans and 29.35 eV for high-resolution scans. The pressure in the analysis chamber was maintained below \(5 \times 10^{-8}\) Pa for data acquisition. The data was processed using Multipak software, version 9.6.0. The XPS data was internally referenced to the C-C C1s peak (BE for C-C of 284.78 eV). The optical transmission was measured using a Cary 500 spectrophotometer in the wavelength interval from 400 nm to 2800 nm. Studies of the effects of illumination on the surface voltage were taken using surface photovoltage (SPV) technique in the energy range of 0.5 – 5.0 eV.

Thick films on glass substrates were deposited by flash evaporation technique from previously prepared ingots of haycockite CuFeS\(_2\). Morphology of thin films and their chemical composition were investigated using the Hitachi TM3000 Tablopt Microscope equipped by Energy Dispersive Spectrometer (EDS). The magnification was varied from \(\times 50\) to \(\times 10000\). The X-ray studies were carried out using monochromatic Cu K\(\alpha\) radiation (1.5406 \(\AA\), step size 0.01\(^\circ\) or 0.04\(^\circ\), counting time 10 s). The Retrived analysis of the X-ray powder diffraction data was done using the FullProf software. X-ray photoelectron spectroscopy (XPS) measurements were performed with PHI 5000 VersaProbe II XPS system using a monochromatic Al K\(\alpha\) source (15 kV). The pass energy was 117.4 eV for survey scans and 29.35 eV for high-resolution scans. The pressure in the analysis chamber was maintained below \(5 \times 10^{-8}\) Pa for data acquisition. The data was processed using Multipak software, version 9.6.0. The XPS data was internally referenced to the C-C C1s peak (BE for C-C of 284.78 eV). The optical transmission was measured using a Cary 500 spectrophotometer in the wavelength interval from 400 nm to 2800 nm. Studies of the effects of illumination on the surface voltage were taken using surface photovoltage (SPV) technique in the energy range of 0.5 – 5.0 eV.

It was found that thin films have the chemical composition with the atomic content of Cu, Fe, and S of 25.21, 27.77, and 47.02 at. % with the atomic ratios of Cu/Fe and S/(Cu + Fe) equaling to 0.91 for the atomic ratio Cu/Fe and 0.90 for the atomic ratio S/(Cu + Fe) while these theoretical values for haycockite CuFeS\(_2\) are equal to 0.80 and 0.89 respectively. Thin films of chalcopyrite consist of separate grains with the approximately equal areas of about \((1000 – 2000)\) \(\mu\)m\(^2\). It may be proposed that this structure appeared during cooling thin films because it completely covers the surface of thin films. The small inclusion of the second phase with the chemical composition close to talnakhite CuFeS\(_2\) was detected. The most common occurrence of the inclusion of the second phase along the borders of grains was equal to about \((1000 – 2000)\) \(\mu\)m\(^2\) which is the presence of Se\(_{3d}\) peak on the composition of the solid solutions were investigated and explained by the binding behavior of the Se atoms in the (CuGaSe)\textsubscript{x}(CuAlSe)\textsubscript{1-x} system. There was a correlation of the Raman active modes with the change in chemical composition of this system.

The untreated, chemically etched, and Ar\(^{+}\)-sputtered surfaces of single crystals were investigated, and the effects of chemical etching and then Ar\(^{+}\) sputtering on the same surface of a crystal were determined. The spectra of the untreated samples showed a typical oxidized surface, strong O1s and C1s signals. The Se3d spectra revealed an additional component (Se\textsuperscript{2-}\(^{\pm}\)) due to the existence of Se\(_2\)O\(_2\) at the surface of the untreated samples. An additional signal corresponding to I\(_{3d3,2}\) at 619.1 eV was detected, showing the presence of single crystals of CuI on the surface of the untreated samples. Chemical etching for 30 s, the oxygen and carbon contamination at the surface was removed. After the treatments, no detectable lattice damage was observed. The change of parameters of Ar\(^{+}\) sputtering from 4 mm\(^2\), 2 kV, 1 \(\mu\)A to 5 kV, 25 mA, resulted in the appearance of an Al sub-peak corresponding to the neutral state of Al.

The position and shape of the Se3d peak on the composition of the solid solutions were investigated and explained by the binding behavior of the Se atoms in the (CuGaSe)\textsubscript{x}(CuAlSe)\textsubscript{1-x} system. There was a correlation of the Raman active modes with the change in chemical composition of this system.

The recent efficiency advances in solar cells based on Cu\(_2\)ZnSnS\(_4\) (CZTS) have raised hopes for reaching high efficiency and low cost with robust and durable devices. However, in fabrication of monolithic CZTS/Si tandem structures, two major problems must be overcome: 1) a proper interlayer between top and bottom cell has to be developed, since the tunnel junctions typically used in III-V tandem cells are not trivially available, and 2) unlike in their Perovskite/Si tandem counterpart, the processing of the CZTS top component (Se\(_{3d}\)) is equally to 0.91 for the atomic ratio Cu/Fe and 0.90 for the atomic ratio S/(Cu + Fe) while these theoretical values for haycockite CuFeS\(_2\) are equal to 0.80 and 0.89 respectively. Thin films of chalcopyrite consist of separate grains with the approximately equal areas of about \((1000 – 2000)\) \(\mu\)m\(^2\). It may be proposed that this structure appeared during cooling thin films because it completely covers the surface of thin films. The small inclusion of the second phase with the chemical composition close to talnakhite CuFeS\(_2\) was detected. The most common occurrence of the inclusion of the second phase along the borders of grains was equal to about \((1000 – 2000)\) \(\mu\)m\(^2\) which is the presence of Se\(_{3d}\) peak on the composition of the solid solutions were investigated and explained by the binding behavior of the Se atoms in the (CuGaSe)\textsubscript{x}(CuAlSe)\textsubscript{1-x} system. There was a correlation of the Raman active modes with the change in chemical composition of this system.

Acknowledgment. B. Korzun would like to thank PSC-CUNY for financial support of the studies under project TRADA-49-552.

SESSION ES20.04: Specific Material
Session Chairs: Daniel Lincot and Sascha Sadewasser
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 132 B

8:30 AM *ES20.04.01
Monolithic Tandem Solar Cell Potential of CZTS on TOPCon Si
Filipe Martinho, Alireza Hajijafarassar, Simon Lopez-Marino, Moises Espinola-Rodriguez, Stela Canuelsen, Eugen Stamate, Mungunshagai Gansukh, Sara Engberg, Ole Hansen, Andrea Crovetto and Jorgen Schou; Technical University of Denmark, Roskilde, Denmark.

The recent efficiency advances in solar cells based on Cu\(_2\)ZnSnS\(_4\) (CZTS) and related high bandgap alloys make them promising compounds for application in tandem cells, in particular when monolithically integrated with a Si-based bottom cell, with the prospect of an all earth abundant, stable, efficient and industrially feasible tandem solar cell. However, in fabrication of monolithic CZTS/Si tandem structures, two major problems must be overcome: 1) a proper interlayer between top and bottom cell has to be developed, since the tunnel junctions typically used in III-V tandem cells are not trivially available, and 2) unlike in their Perovskite/Si tandem counterpart, the processing of the CZTS top cell involves at least one high temperature step (>500 C) which must not damage the bottom Si cell structures nor contaminate them with elements such as Cu or S diffusing from CZTS.

In this contribution, we approach these problems by using a thermally resilient n-type Si Tunnel Oxide Passivated Contact (TOPCon) bottom structure with a thin (<25 nm) TiN layer at the interface between the top and bottom cells, serving both as diffusion barrier and recombination layer. Using Microwave Detected Photoconductance Decay (\(\mu\)-PCD) and Secondary Ion Mass Spectrometry (SIMS), we that a regime for CZTS production exists where contamination of the bottom Si cell is kept at low levels, with post-process carrier lifetimes exceeding 1.5 ms, corresponding to an implied Voc (iVoc) of above 700mV. Based on these findings, we develop and characterize a series of monolithic CZTS/Si tandem devices with different interface configurations and barrier layer thicknesses. We discuss the optical impact of the different tandem interfaces used on the overall tandem performance. Moreover, we compare the photovoltaic properties of the CZTS films used as the top cells with our single junction CZTS baseline, based on co-sputtering. Although a natural trade-off exists which narrows down the processing regimes necessary to simultaneously achieve efficient top and bottom cells, our results do not reveal any priori fundamental limitations to achieving efficient monolithically integrated CZTS/Si tandem solar cells.

9:00 AM ES20.04.02
Development of CIS and Perovskite Solar Cells for all Thin-Film Tandem Applications
Thomas Feurer\(^1\), Stefano Pisoni\(^2\), Thierry Moser\(^1\), Yan Jiang\(^1\), Fan Fu\(^2\), Romain Caron\(^1\), Shiro Nishiwaki\(^1\), Stephan Buecheler\(^2\) and Ayodyha N. Tiwari\(^3\); Empa-Swiss Federal Laboratories for Materials Science and Technology, Dubendorf, Switzerland; \(^2\)Photovoltaics and Thin Film Electronics Laboratory (PV-LAB), EPFL, Neuchatel, Switzerland.
For all thin film tandem configuration, perovskite and Cu(In,Ga)Se₂ (CIGS) solar cells represent ideal candidates for top and bottom devices due to their suitable energy band gaps. In this contribution we will show how CuInSe₂ (CIS) based absorbers can be pushed from 15% to beyond 19% without changing the optical bandgap of 1.0 eV. To do so we suppress back contact recombination by adding a graded composition to the back interface, increase carrier lifetime by additional post deposition treatment and increase absorber quality by shifting to a more stoichiometric composition between Cu and group III elements. Combined with semitransparent perovskite top cells we demonstrate efficiencies above 24% in four-terminal tandem configuration on rigid substrate. Further, the possibility to develop highly efficient perovskite and CIGS solar cells on flexible substrates lays the foundations to lightweight flexible tandem devices by high-throughput roll-to-roll manufacturing. We present a multistage vacuum-solution deposition method for perovskite absorber to tailor PbI₂ growth morphology. With this approach, we demonstrate a steady-state efficiency of 14.0% for NIR-transparent perovskite solar cells (average transmittance of ~74% between 800 and 1000nm), on a flexible front sheet which is used for flexible CIGS module encapsulation. Flexible perovskite/CIGS tandem with 19.6% efficiency is obtained in four-terminal configuration. Our work represents a step forward towards highly efficient low band gap CIS solar cells and provides insights into growth of layers and interfaces for high efficiency flexible perovskite solar cells. Furthermore, latest results on both four-terminal as well as monolithic two-terminal thin film tandem devices will be discussed.

9:15 AM ES20.04.03
Zn₁₋ₓMgₓO Contact Layer Integration with Wide Band Gap CuGaSe₂ Absorbers
Imran S. Khan¹, Christopher Muzzillo², Craig Perkins³, Nicolas Gaillard⁴ and Andriy Zakutayev⁵; ¹National Renewable Energy Laboratory, Lakewood, Colorado, United States; ²University of Hawaii, Honolulu, Hawaii, United States.

CuGaSe₂ thin film is polycrystalline thin band gap material related to chalcopyrites. It is a promising absorber candidate for top cell application in both for tandem photovoltaic (PV) solar cells and photoelectrochemical (PEC) water splitting devices. Zn₁₋ₓMgₓO is an attractive n-type contact layer for CuGaSe₂ and other PV absorber technologies due to its tunable conduction band offset as a function of Mg concentration. In this study, Zn₁₋ₓMgₓO is being investigated as the buffer/contact layer for CuGaSe₂ based PV and PEC devices.

CuGaSe₂ thin films with Cu/Ga = 0.36 composition are deposited by single-stage co-evaporation, and Zn₁₋ₓMgₓO films are deposited using combinatorial RF sputtering. The electrical, optical and structural properties of the Zn₁₋ₓMgₓO films as function of Mg compositions are characterized. A baseline device is fabricated in a similar fashion to CIGS devices, with CdS window layer and i-ZnO buffer layer. Zn₁₋ₓMgₓO is studied as replacement for both CdS and i-ZnO, and is grown as as-deposited, water-treated, and Cd²⁺ solution treated CuGaSe₂ absorber thin films. X-ray photoelectron spectroscopy (XPS) is performed on the treated films to study the surface defect chemistry.

The resulting CuGaSe₂/Zn₁₋ₓMgₓO device JV and EQE performance is observed to be dependent on the temperature and the duration of the treatments. Replacing CdS/i-ZnO with Zn₁₋ₓMgₓO improves the carrier collection in the short wavelengths due to the higher bandgap of Zn₁₋ₓMgₓO. The measured device performances are directly related to the Zn/Mg ratio in the contact layer, and supports the significance of conduction band optimization. Open circuit voltage up to 920 mV is measured, which is important for PEC water splitting and tandem PV application.

9:30 AM *ES20.04.04
Studies on MoS₂ Thin-Film Matrix by Meaning of Atom Probe Tomography
Manuel A. Ramos¹, ², John Nogán², Jose L. Enríquez-Carrejó², Claudia A. Rodríguez-González³, Roberto C. Ambrosio-Lazaro¹, Torben Böhl¹, Delphine Chassaing¹, Martin Heinmaier² and Sandra Kauffmann-Weiss³; ¹Universidad Autonoma de Cd. Juarez, Cd. Juarez, Mexico; ²Integration, Center for Integration of Nanotechnologies, Albuquerque, New Mexico, United States; ³Ciencias Básicas, Facultad de Ciencias de la Electrónica, Puebla, Mexico; ⁴Institute for Technical Physics, Karlsruhe Institute of Technology-Institute for Applied Materials, Karlsruhe, Germany.

A characterization study using atom probe tomography to understand crystal growth and other micro-structural aspects on molybdenum di-sulfide (MoS₂) thin films is presented in this paper. The film was deposited on silicon dioxide (SiO₂) coupons using radio frequency at 275W at high vacuum~10⁻⁹ from commercial MoS₂ 99.9% purity target. From scanning electron microscopy, it was possible to observe vertically crystal growth with high-porosity and three-dimensional reconstruction from spatial distribution from atom probe tomography indicates low impurities and no grain boundaries within molybdenum disulfide crystallites on film matrix. As complementary, electrical transport -3V to 3V at room temperature and X-ray pole figures were also measured on the films to understand crystal grain orientation.

10:00 AM BREAK

SESSION ES20.05: Interface and Material
Session Chairs: Thomas Feurer and Filipe Martinho
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 132 B

10:30 AM *ES20.05.01
Progress and Challenges in Absorber and Interface Fabrication of Polycrystalline CdTe Photovoltaics
Amit H. Munshi¹, Jason M. Kephart², Ali Abbas³, Thomas Fiducia², Adam Danielson¹, Carey Reich¹, Tushar Shimpi¹, John M. Walls⁴ and Walajabad Sampath¹; ¹Mechanical Engineering, Colorado State University, Fort Collins, Colorado, United States; ²CREST, Loughborough University, Loughborough, United Kingdom.

Polycrystalline thin-film CdTe device efficiency of over 19% has been demonstrated at Colorado State University using a repeatable and scalable sublimation process. Record efficiency for research scale CdTe photovoltaics has been reported to be over 22% and highest reported module efficiency is over 18% by First Solar Inc. Use of Se alloying with CdTe to form a lower band-gap CdSe₄Te₅, (CST) alloy has led to higher devices efficiencies with better current collection. Recent materials characterization has revealed that Se may be responsible for more than just reduction of band-gap. With CdCl₂ treatment Cl₁ is known to very effectively passivate defects at CdTe grain boundaries. Recent materials and electrical characterization have shown that Se has a very similar behavior to Cl₁ at the grain boundaries of polycrystalline CdTe. These include Se decorating the grain boundaries like Cl₁ in the while cross-section cathodoluminescence maps show substantially higher signal intensity in regions with Se. Double heterostructures fabricated using CdS/CdTe with Al₂O₃ as a passivating oxide have been measured to have several hundred nanosecond bulk recombination lifetime. These films were also measured to have surface recombination velocity of under 100 cm/s. These results among others emphasize that Se also helps in passivation of grain boundaries. High absorber quality may help in mitigating voltage deficit that has traditionally been the largest limiting factor in CdTe photovoltaics in achieving efficiency closer to Shockley-Queisser limit. In addition to graded absorber devices and double heterostructures, replacing the traditional Cu doping with more advanced group V doping is an important research effort that maybe critical for future improvements in device efficiency. Nitrogen, Phosphorous, Arsenic and Antimony doping has been investigated by several research groups. Advanced co-sublimation hardware developed at Colorado State University a unique capability of depositing films for group V doping under over pressure of Cd. Such deposition under Cd overpressure causes formation of V₂, that is known to be favorable for incorporation of group V dopant and activation. Utilizing the high absorber and interface quality material and higher doping, efforts are in progress to fabricate polycrystalline devices with open-circuit voltage over 1 and device efficiency over 20%.

11:00 AM ES20.05.02
Introduction of K From the Back Electrode in an All-PVD Ag-CIGS Manufacturing Process
Dmytro Poplavskyy, Roun Farshevi, Neil Mackie, Ben Hickey and David Spaulding; MiaSolé Hi-Tech, Santa Clara, California, United States.

We report on simultaneous incorporation of sodium and potassium in the absorber layer of all-sputtered Ag-CIGS solar cells fabricated in a MiaSolé roll-coater multi-chamber manufacturing tool. The MiaSolé process begins with a stainless-steel substrate, which is unwound into the roll-coater where the following layers are consecutively deposited by sputtering: diffusion barrier layer, alkali-doped Mo back electrode, absorber layer, CdS buffer layer, and TCO window layer. Addition of potassium to the absorber has been reported to lead to higher cell efficiency, and in the majority of cases potassium is introduced via a post-deposition treatment (typically as KF, after CIGS deposition). In the MiaSolé process, both sodium and potassium are introduced from the molybdenum back electrode, which is sputter-deposited from Mo rotary targets, doped with sodium and potassium molybdates, respectively. Changing the sputter deposition power and varying the depth of the doped layer inside the Mo electrode allows us to vary the amount of alkali
metals delivered to the absorber. Addition of the K-doped back electrode to the Na-doped Ag-CIGS baseline process leads to a higher solar cell efficiency (up to 0.5%abs), mostly driven by higher FF and Voc as a result of reduced interfacial recombination and reduced voltage dependent collection losses. Auger electron spectroscopy (AES) and secondary-ion-mass spectroscopy (SIMS) results indicate that potassium primarily accumulates near the main junction and leads to reduced Cu/(Ga+In) in that region, similarly to observations reported in the literature. However, in contrast to numerous reports, we do not observe any evidence for the formation of secondary phases, such as e.g. K-In-Se, according to x-ray photoelectron spectroscopy (XPS) measurements.

In the Misaéinline sputtering process, the last stage of the absorber growth converts the absorber film to a Cu-poor composition via sputtering from targets with reduced Cu content. We demonstrate that lower surface Cu content is required for high efficiency in the presence of potassium. Furthermore, the degree of potassium accumulation at the junction appears to increase linearly with decreasing Cu/(Ga+In) ratio in that region and correlates with increased cell efficiency.

Flexible modules made from the optimized baseline (Na-only) and K-doped (Na+K) cells yield comparable light-soaking (24 hours under 1 sun) and accelerated damp-heat (85°C/85%RH at 1000hrs) performance suggesting no adverse impact of introduction of K on module reliability.

11:15 AM ES20.05.03
P-Type Hydrogenated Amorphous Silicon—A Hole-Selective Contact to Cadmium Telluride Based Solar Cells
William Weigand1, Carey Reich2, Amit H. Munshi3, Arthur Onno4, Adam Danielson5, Walajabad Sampath6 and Zachary Holman7; 1Arizona State University, Tempe, Arizona, United States; 2Colorado State University, Fort Collins, Colorado, United States.

In recent years, the quality of cadmium telluride based solar cells has increased with efficiencies exceeding 22%. This high efficiency can be attributed to the improved bulk quality of the CdTe bulk. As with silicon-based solar cells, an improved bulk quality warrants the development of a passivating and carrier-selective contact structure that is capable of extracting holes and repelling electrons or vice-versa. Such a structure has already been well-developed for silicon based solar cells through the implementation of an amorphous silicon (a-Si:H) based contact structure and is the basis of the highest efficiency silicon solar cell to date. In the CdTe world, a similar contact based on p-type a-Si:H on monocrystalline CdTe produced a open-circuit voltage of greater than 1 V indicating the potential of a-Si:Hp) to act as a hole-selective contact. Ultimately, the fill factor of this high Voc device was fairly low at 65.5%—one of the major requirements for a passivating and carrier-selective contact—indicating that the contact stack may not be majority-carrier conductive. Furthermore, the Voc of this device was fairly low at 65.5%.—one of the major requirements for a passivating and carrier-selective contact—indicating that the contact stack may not be majority-carrier conductive. Finally, the fill factor of this device was relatively low with a value of 65.0% indicating that the a-Si:Hp contact stack is not currently majority-carrier conductive. By manipulating the interface and bulk properties of our a-Si:H(p) based stack we show that a-Si:H(p) can indeed act as a carrier-selective contact to solar cells based on CdTe and its alloys.

11:30 AM ES20.05.04
Determining the Properties of Cd1-xInx2-4δS4+a Thin Films—A Key to Better Understand CIGSe/CdS Heterojunction?
Nicolas Barreau1, Thomas Lepetit2, Pawel Zabierowski3, Ludovic Arzel4, Camille Latouche5, Sylvie Harel5 and Stéphane Jobic1; 1Institut des Matériaux Jean Rouxel (IMN), Nantes, France; 2Warsaw University of Technology, Warsaw, Poland.

The optoelectronic properties of CdInS4 spinel single crystal have been widely investigated until the end of the 1980s. Interestingly, these studies report the presence of defect levels which usually lie in the band gap strongly depends on cationic In-Cd exchanges in the tetrahedral sites. Since a compound derived from this phase is suspected to be formed at the interface between KF-treated Cu(In,Ga)Se2 and (CB/CD)S, re-investigating this material as thin film makes sense and is the purpose of the present contribution. Thin films of Cd1-xInx2-4δS4+a, with x going from 0 to 1, were grown through the co-evaporation of indium, sulfur and CdS. The fluxes of indium and CdS were adjusted so that films of the following compositions could be achieved: x=0 (CdS), x=0.6 or x=1 (InS). Those 325±5 nm-thick layers were deposited on glass substrates heated at 400°C. The structural properties of these thin films were investigated by X-ray diffraction; they all crystallize in the spinel structure, but the cationic disorder could hardly be determined. All of these films were also characterized optically; they showed an absorption coefficient with incident energy is strongly dependent on x. Their electrical characteristics were investigated through Hall-effect measurements, temperature dependence of conductivity, and photoconductivity. In addition, the formation energies of point defects were theoretically evaluated by DFT. These studies all converge toward the conclusion that the optoelectronic properties of Cd1-xInx2-4δS4 strongly depend on x (which is likely to imply cationic disorder), but most probably also on another parameter difficult to control, that is sulfur deficiency. To explore this latter parameter, all kinds of films (x=0, 0.6 or 1) were annealed for 72h at 300°C in an evacuated sealed tube with or without additional sulfur pellets. Thereby, the parameter δ (denoting the amount of sulfur vacancies) could be qualitatively investigated. The films obtained, Cd1-xInx2-4δS4, were also structurally, optically and electrically characterized. The conclusion of these investigations is that there exists a complex correlation between Cd/(In ratio and the amount of S vacancies, strongly influencing defects level distribution within the band gap of this spinel.

The structural and optoelectronic characterizations of these thin films lead us to conclude that the electronic nature and distribution of the defect levels is dependent on both x and δ. This may explain the electronic properties of these materials diversely wavelength dependent. Such a conclusion is likely to provide new bricks to the understanding of CIGSe/CdS hetero-junction photovoltaics.

11:45 AM ES20.05.05
ALD-ZnTiO as Window Layer in Cu(In,Ga)Se2 Solar Cells
Johannes Loeckinger1, Shiro Nishiwaki2, Christian Andres3, Stephan Buecheler4, Yaroslav E. Romanyuk5 and Ayodhya N. Tiwari; Empa–Swiss Federal Laboratories for Materials Science and Technology, Duebendorf, Switzerland.

The most commonly applied buffer layer in photovoltaic devices employing Cu(In,Ga)Se2 is CdS. The parasitic optical absorption of CdS (Eg = 2.4 eV) results in a reduced photocurrent density. A simple reduction of the CdS layer thickness, however, leads to a reduced device performance due to a loss in open-circuit voltage (Voc) attributed mainly to insufficient coverage on the rough surfaces and possible sputter damage of the CISG absorber surface during the deposition of the window layer. In this contribution an alternative window layer is presented replacing the sputtered Zno. Highly resistive and transparent ZnTiO is deposited by atomic layer deposition (ALD) onto the substrate/Mo/CIGS/CdS stack. The finished devices are then characterized by current-voltage and external quantum efficiency (EQE) measurements. ALD is chosen for this purpose since for thin and resistive oxide layers a conformal coverage of the rough surface and a precise thickness control are paramount. Further, ALD allows for a compositional grading of ZnTiO at a nanometer scale. It is found that with ALD-ZnTiO instead of sputtered Zno the CdS thickness can be reduced without adversely affecting the Voc (~0.7 V) and therefore a gain in current density (~0.8 mA cm−2) from a reduced parasitic absorption of both CdS and Zno is achieved. Temperature dependent I-V measurements and its correlation with the FF support the benefit of a compositional grading of ZnTiO.

SESSION ES20.06: Material Characterization
Session Chairs: Dirk Hauschild and Takehiko Nagai
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 132 B

3:30 PM *ES20.06.01
Different Alkali-Fluoride Post-Deposition Treatments of Cu(In,Ga)Se2 Investigated by Kelvin Probe Force Microscopy
Nicoletta Nicolara, Rody Manaligod, Philip Jackson, Dimitrios Hariskos, Giovanna Sozzi, Roberto Menozzi, Wolfiam Witte and Sascha Sadawasser; 1International Iberian Nanotechnology Laboratory, Braga, Portugal; 2SW, Stuttgart, Germany; 3University of Parma, Parma, Italy.

A series of efficiency improvements of Cu(In,Ga)Se2 (CIGSe) thin-film solar cells have been achieved over the last 7 years by the development of alkali-fluoride post-deposition treatments (PDT) [1]. These processes modify the optoelectronic properties of CIGSe providing an improved surface for subsequent buffer growth by chemical bath deposition (CBD) [2,3] and favoring a reduction of the buffer thickness, as compared with non-PDT interfaces [4]. We present a Kelvin probe force microscopy (KPFM) study of the influence of different alkali-fluoride PDTS on the CIGSe absorber surface properties and the interface formation
to the CBD buffer layers. The surface potential variation at more than 200 grain boundaries was measured, allowing for a meaningful statistical analysis. A strong difference for different alkali elements (K, Rb, and Cs) is found, which shows a clear correlation to the open-circuit voltage of reference solar cell devices. For the KD-PDT samples strong variations in the potential at the grain boundaries are observed, exhibiting large hole and electron barriers, whereas for RbF and CsF we only observe small electron barriers and neutral grain boundaries, suggesting an effective passivation effect.

For the interfacial formation between co-evaporated CIS layers subjected to a RbF-PDT with the solution-grown buffer layers CdS and Zn(O,S) we studied the evolution of the work function with increasing buffer layer thickness. Information about effective charge carrier separation at the forming interface was obtained from positive surface photovoltage (SPV) measurements. Surprisingly, for the Zn(O,S) buffer layer a negative SPV was found, which could be explained with the help of simulations by the presence of acceptor-type defects at the surface of Zn(O,S).

Our KPFM results provide valuable insights for the further improvements of CIS solar cell efficiencies.


4:00 PM ES20.06.02
Role of Alkali Metals at Grain Boundaries of Cu(In,Ga)Se2 Thin Films

Daniel Abou-Ras1, Aleksandra Nikolaeva1, Sebastian Caiicedo Davila1, Marcin Morawski2 and Roland Scheer; 1Helmholtz-Zentrum Berlin, Berlin, Germany; 2Institute of Physics, Photovoltaics Group, Martin-Luther-Universit ät Halle-Wittenberg, Halle, Germany.

Currently, the Cu(In,Ga)Se2 (CIGSe) solar-cell devices exhibiting highest conversion efficiencies of close to 23% have been fabricated using polycrystalline absorber layers which contained alkali metals already during or after which alkali metals were introduced via a postdeposition treatment (see, e.g., Ref. 1). The beneficial effects of alkali metals on the materials and device properties of CIGSe solar cells are diverse, and it is convenient to divide them into those affecting the bulk properties (such as the net doping density of the CIGSe layer), as well as into those acting at the interfaces to the films (such as the net doping density of the CdS layer). Surprisingly, for the Zn(O,S) buffer layer a negative SPV was found, which could be explained with the help of simulations by the presence of acceptor-type defects at the surface of Zn(O,S).

Our KPFM results provide valuable insights for the further improvements of CIGSe solar cell efficiencies.


4:15 PM ES20.06.03
Ultra-High Vacuum Scanning Tunneling Spectroscopy on CuInSe2 Thin-Film Solar Cell Absorber Layers

Karien Kameni Boumengo1, Thiibaut Gallet1, Evandro Lanzoni2, Finn Babbe1, Michele Melchiorre1, Conrad Spindler1, Jérôme Guillot2, Susanne Siebentritt1 and Alex Redinger1, 1University of Luxembourg, Luxembourg, Luxembourg; 2Luxembourg Institute of Science and Technology, Belvaux, Luxembourg.

Polycrystalline Cu(In,Ga)Se2 (CIGS) appears nowadays as one of the most promising candidates for the fabrication of high efficiency thin film solar cells. However, the current record efficiency (22.9% [1]) is still lower than the one of the single crystalline GaAs thin film solar cells (28% [1]). The discussion about whether this lower performance is attributed to the nature of the surface or grain boundaries (GBs) electronic properties is still ongoing [2].

In this work, we investigated the surface and grain boundary properties of CuInSe2 (CIS) with scanning tunneling microscopy (STM) and spectroscopy carried out under ultra-high vacuum conditions. This technique enabled us to measure the local density of states (LDOS) with nanometer precision. In particular, we studied the effect of potassium cyanide (KCN) etching, the influence of heating in vacuum and pre-electrolyte treatment with CdS and NH4OH. We found that in both cases, the surface is Cu-depleted (in agreement with most reports in literature) and most of the Cd was confined to the first few nanometers. We measured signatures of a defective surface with a high density of surface states, which can be improved, to a certain extend via an UHV annealing to 280°C [4]. However, in CIGS solar cells the heterojunction is usually made with CdS and consequently we studied the absorbers after a Cd-pre-electrolyte treatment. This enabled us to expose the surface to a high amount of Cd2+ ions without actually growing a CdS layer, which would render an investigation of the CIS surface with STM impossible.

Interestingly, the surface electronic properties are changing substantially after the Cd2+ treatment, and we observed (a) less inhomogeneities and (b) a reduction of the surface defect density, which manifested itself by a shift in the Fermi-level at the surface. Compared to the KCIS samples we do not observe distinct features at the grain boundaries anymore.

XP measurements gave important insights into the changes of the surface composition after the various treatments. We observed an Indium depletion on the Cd2+ CIS compared to the KCIS samples, which suggests that the Cd ions are substituting Indium at the surface. We compared the surface compositions to the compositions after mild sputtering with Argon ions. We found that in both cases, the surface is Cu-depleted (in agreement with most reports in literature) and most of the Cd was confined to the first few nanometers.

The PL measurements on both types of samples (KCS vs Cd2+ CIS) showed no considerable change on the bulk electronic properties. A detailed analysis of these observations will be presented and discussed.

Reference
reported that the interdiffusion of Cu and In/Ga between CIGS and Cu-Se layers is essential for the grain growth of CIGS during this Cu-poor to Cu-rich transition\textsuperscript{1-5}. However, little has been known about how the atomic structures evolve during this process.

In the present study, we use the CuInSe\textsubscript{2} (CIS) system, as it is simpler than CIGS for an initial study. Cu-Se was deposited on top of CIS, and the grain growth was directly monitored during in-situ heating in a scanning electron transmission microscope (STEM). The compositional changes were revealed simultaneously with electron energy-loss spectroscopy (EELS). The corresponding time-series STEM images and elemental maps will be presented in the conference. The results show that planar defects play an important role in grain growth. The grains with high-density planar defects tend to be consumed by the grains without planar defects, and this does not occur when there is no extra Cu-Se layer deposited on CIS. Simultaneously acquired STEM images and EELS spectrum images reveal that Cu-rich grain boundaries (GBs) between highly defected and non-defected CIS grains migrate towards the highly defected CIS grains during heating. Further EELS elemental mapping reveals Cu enrichment and In depletions at most GBs within regions having widths of more than 10 nm. Atomically resolved STEM images show a gradual phase change from a chalcopyrite CIS structure at CIS grain interiors towards an antiferroelectric Cu\textsubscript{2}Se structure at GBs, which is also evidenced by atomic-resolution EELS. In this gradual phase change, the Se sublattice stays the same, while In and Cu interdiffuse gradually without any dislocations between the Cu\textsubscript{2}Se and CIS phases. Moreover, In atoms are found at interstitial sites in Cu\textsubscript{2}Se near GBs. Density functional theory (DFT) calculations show that the diffusion barrier of In atoms from interstitial to interstitial sites in Cu\textsubscript{2}Se is very low. These results not only show that Cu diffusion at GBs assists the recrystallization of CIS, but also reveal the mechanism beneath it, which will be discussed at the conference.

Acknowledgment: Research funded in part by the Helmholtz Virtual Institute "Microstructure Control for Thin-Film Solar Cells", VH-VI–520 project. CL acknowledges the support from Max Planck Society.

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conversion efficiency of 4% has been achieved for an alkali-free absorber, which is on the order of the non-doped record cell by Tiwari et al., [1]. The $V_{OC}$ was 580 mV, which lags behind the record pure-sulfide CZTS device of 683 mV, [2], and suggests that there is room for improvement.

In this work, we screen the effect of incorporating various types of new cations into the kesterite, including Ag and Ba by direct addition into the precursor ink. A comparison will be given in terms of the structure, morphology, and opto-electronic properties.


ES20.07.03
Fabrication of Band-Gap Graded CZTSSe Thin-Film Solar Cells Teoman Taskesen, Devendra Pareek, David Nowak, Timo Pfeiffelmann and Levent Güttay; University of Oldenburg, Oldenburg, Germany.

The tunability of the band-gap in kesterite absorbers by choosing different S/Se ratios offers the possibility to create a band-gap gradient throughout a single absorber layer of Cu2ZnSn(S,Se)4. This type of band-gap gradient is deeply investigated for CIGS technologies where it is commonly used for a significant enhancement of the device performance, by allowing for combination of optimized optical properties and reduction of charge carrier recombination. In this work, we present a novel method for introducing a band-gap grading via sulfuration of pure selenide Cu2ZnSnSe4 thin films by using hydrogen sulfide (H2S). The impact of various process parameters of H2S assisted sulfuration such as pressure, temperature, and duration on the properties of the resulting Cu2ZnSn(S,Se)4 absorbers are discussed. In particular, the elemental S/Se gradient throughout the sample after the process, the total content of sulphur as well as its impact on absorber band-gap and quality are investigated. Raman depth profiling confirms the formation of a grading with a relatively high sulphur concentration at the front surface which decreases towards the back side of the absorber, resulting in a front graded Cu2ZnSn(S,Se)4 absorbers. The results indicate that selenium depletion from the existing material and S-Se exchange are taking place simultaneously during the process, affecting also material properties other than the grading profile. Inaccurate selection of process parameters outside a stable range can lead to decomposition of the Cu2ZnSnSe4 layer and the formation of ZnS secondary phase at the absorber surface. Finally, the effects and advantages of the presented H2S assisted process are further discussed, including the strong kinetic nature of this process which appears to allow for a fast incorporation of a sulphur gradient.

Results on solar cell devices will be presented.

ES20.07.04
Over 13% Efficient CZTSSe and CIGS Solar Cells Processed from Non-Hydrazine Solutions Yuancai Gong, Jingjing Jiang, Shaotang Yu, Yifan Zhang, Sanping Wu, Weibo Yan and Hao Xing; Key Laboratory for Organic Electronics and Information Displays, Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), College of Materials Science and Engineering, Nanjing University of Posts & Telecommunications, Nanjing, China.

For thin film solar cells to compete with the current market dominate silicon ones, reducing production cost is the key. Large area solution processing (to replace vacuum based deposition) to reduce fabrication cost and using earth abundant elements to lower materials cost are both effective ways to achieve this goal. Here, we report over 13% efficient copper indium gallium selenide (CIGSs) and copper indium selenide (CZTSs) solar cells respectively fabricated from DMF and DMSO molecular precursor inks. We have first used DMF as single solvent to prepare precursor solution and fabricated 10.3% efficient copper indium selenide (CISs) solar cells without any etching. We have now systematically investigated the effect of the Cu/In ratio in the precursor solution on the CISs device performance. We found that solar cell performance increases from Cu-poor (0.85) to slightly Cu-rich and then decreases for further Cu-rich condition with a peak conversion efficiency (PCE) of 12.20% achieved from the Cu/In ratio of 1.05. Further, by gallium alloying, CISs solar cell with a PCE of 13.6% has been fabricated under similar Cu-rich (Cu/In(Ga)=1.05, Ga/(In+Ga)=0.2) condition. Our results for the first time demonstrate highly efficient CIS/CIGS solar cells can be achieved from absorbers grown under Cu-rich condition. Characterization of the absorber materials and solar cell devices are investigated to understand the mechanism behind the phenomenon observed. The main issue for CZTS solar cell further development is the large open-circuit voltage deficit ($V_{oc-def}$) which could be due to large tail states, Cu-Zn antisite order-disorder, formation of deep defects and interface recombination. DMSO precursor solution has been demonstrated to be a promising approach for fabricating high performance CZTSs solar cells. Here, we have explored different approaches to understand the $V_{oc-def}$ of DMSO based CZTSSe solar cells. First, we found device $V_{oc}$ (as well as efficiency) is strongly affected by the precursor tin oxidation state (Sn4+/Sn2+) in the precursor solution. A PCE of 13.2% has been achieved from Sn4+ solution with a $V_{oc-def}$ of only 0.570 V, much lower than the current world record CZTSSe device (0.617 V), whereas the efficiency obtained from Sn2+ solution was only 7% with $V_{oc-def}$ higher than 0.600 V. The reason for the huge difference has been investigation by solution chemistry, film morphology, material property and device characterizations. Second, we have found that Ag or Ge alloying have positive effect on the $V_{oc-def}$ of DMSO solution processed CZTSSe solar cells. Our results shed new lights on suppressing the $V_{oc-def}$ and improving the efficiency of CZTSs solar cells.

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ES20.07.05
Impact on Selenium Control at Growth and Annealing for Cu2ZnSnSe4 Solar Cells Hitoshi Tampo, Shinho Kim, Hajime Shibata and Shigeru Niki, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Kesterite Cu2ZnSnSe4 (CZTSe) based materials belong to I-IV-VI4 quaternary compound semiconductor and the composition control is relatively complicated. However, the composition control is very important to obtain high efficiency solar cells. Actually, a specific composition of Cu-poor and Zn-rich composition have been used for high efficiency solar cells, while the off-stoichiometric composition results in formation of many defects. In order to overcome the problem, the several methods are introduced to relieve the off-stoichiometric effect. As mentioned above, the composition control is important however, they are mainly on cation elements, and selenium control has not been so seriously considered compared to these composition controls. One of the reasons is that the selenium control has a small effect on the composition, however selenium related defects are considered to play an important role on electrical properties. In this study, we investigate the impact on the selenium control at growth and annealing, and demonstrate high efficiency of CZTSe solar cells through the selenium control.

To obtain high quality CZTSe thin films, many researchers use two step growth method; first one is precursor deposition or low temperature compound growth, and second one is annealing. In this study, CZTSe thin films were grown by a coevaporation method at 340°C using molecular beam epitaxy equipment, and the selenium supply was controlled with the annealing condition. The annealing temperature was also conducted controlling selenium heating temperature by a quartz tube furnace with three heating zones. Although closed type annealing, at which sample is sealed in a box, is widely used, however, we used an “open type” annealing system, which has higher flexibility to control the annealing conditions, environmental species and its amount with independence from the treatment temperature, treatment pressure, carrier gas flow, and so on.

We investigated the effects of selenium supply both at the growth and annealing, and found that the efficiency gradually decreased for the higher selenium supply at the growth, on the contrary, the efficiency drastically decreased for the lower selenium supply. It was also found that the dependence of selenium supply at the annealing treatment was not so strong compared to that at the growth. The optimal efficiency was obtained with controlling annealing selenium and fixed growth selenium, and conversion efficiency (9.4% -> 10.2% -> 11.6%) improved mainly with Voc (0.401 V -> 0.406 V -> 0.419 V) and FF (0.592 -> 0.647 -> 0.687) in spite of almost constant Jsc (39.6 mA/cm2 -> 38.7 mA/cm2 -> 40.2 mA/cm2). The carrier concentration was almost identical with the conditions and the improvement is considered to be due to reduction of selenium related deep defects. The conversion efficiency of best performing cell 12.0% with Voc=0.418 V, Jsc=42.1 mA/cm2, and FF=0.683.

References:
Effect of Alkali Post-Deposition Treatments on the Cu(In,Ga)Se₂ Surface and the Deeply Buried Cu(In,Ga)Se₂/Mo Interface Structure

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Record efficiencies for Cu(In,Ga)Se₂ (CIGSe) thin-film solar cells have been reached using KF [1], RbF [2], and CsF [3,4] post-deposition treatments (PDT). The underlying mechanism for the observed performance boost have, however, not yet been completely understood. In this contribution, we present the results of hard and soft x-ray photoelectron spectroscopy studies which non-destructively probe the depth-dependent chemical and electronic properties of low-temperature processed CIGSe absorbers as a function of alkali PDT deposition rate. We find a link between Cu depletion at the absorber surface and increasing alkali content, in agreement with Ref. [5]. Depth-dependent valence band photoemission profiles indicate a shift of the valence band maximum (VBM) at the CIGSe surface away from the Fermi level with higher alkali content. It has been reported [6] that alkali elements penetrate into the absorber, especially at grain boundaries as a result of PDT. To investigate potential effects at the back contact, an absorber coated with a combined NaF/RbF/PDT was lifted off the Mo substrate; both sides were studied using hard x-ray photoemission. We detect significant quantities of Rb at the back surface of the absorber, and observe that Rb content is anticorrelated with Na on both front and back CIGSe surfaces. The Cu and Ga depletion resulting from NaF/RbF PDT is seen only at the front side of the CIGSe surface, not at the backside. Furthermore, the spectral shape of the Se and In derived shallow core level lines differs between front and back surfaces, indicating a different chemical structure. Se was found on the Mo substrate after liftoff as a result of MoSe₂ formation at the CIGSe/Mo interface. In our presentation, we will ultimately aim to link our findings to the reported efficiency increase of respective CIGSe solar cells.


A Study of the Degradation Mechanisms of Ultra-Thin CIGS Solar Cells Submitted to a Damp Heat Environment

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On the way to achieve high efficiencies for CuIn₃₋ₓGaₓSe₂ (CIGS) thin film solar cells, alkali doping has become a necessary step. However, it is expected that a migration of the various alkali atoms over the lifetime of the cell will lead to efficiency losses [1]. Logically, ensuring the reliability of a solar cell material is a paramount step towards the commercialization of a product. Indeed, it is necessary for companies to be able to guarantee the efficiencies of the “as-sold” panels over periods of time that expand well over 20 or even 25 years. Experiments studying the reliability of the CIGS and their different components have already been performed in the past [1-4], nevertheless, the exact effects of alkali, and more generally, the precise reasons for, and effect of, the degradation, are still widely unknown.

In order to evaluate the viability of some of the most common techniques used to produce highly efficient thin-film solar cells, ultra-thin coevaporated CIGS solar cell absorber material is produced and doped with various alkali atoms (Na, K, ...). The absorber material is deposited in ultra-thin (400-500nm) layers on soda-lime glass (SLG) equipped with a Si(O,N) diffusion barrier. By reducing the amount of bulk material, the aim is to reduce the concentration of defects in the material and limit their effects as much as possible. The barrier prevents the diffusion of alkali atoms from the SLG into the CIGS and allows for a better control of the concentration of alkali atoms in the layer. Additionally, it allows for a better isolation of the effects of the different alkalis by preventing an uncontrolled mix of alkali from being present in the absorber material.

All alkalis are deposited in their fluoride form (NaF, KF, etc.) either by evaporation, prior to CIGS deposition, or by a post deposition treatment. We monitored the effects of the degradation by regular current-voltage (IV) measurements all along the 1000h experiment. These measurements showed a clear, and alkali concentration dependent, degradation of the solar cells as time increases.

Using Atom Probe Tomography (APT) on degraded as well as on undegraded (reference) cells, it was possible to show that in the absence of a potential, the alkali atom migration is minimal, and that K can be mostly found in the grain boundary region of the absorber material. Given the lack of the expected alkali migration, the main reason for the degradation of the cells seems to be the presence of water that seeps into the grain boundaries of the solar cell material, which could also be observed using APT. The possibility to reverse that degradation mechanisms involving water inclusion is currently under investigation.
Numerical electromagnetic simulations of complete solar cells have been performed for different CIGS thicknesses and various mirror materials. Simulated CIGS absorptions show good agreement with our experimental EQEs, and confirm that parasitic absorption in Mo can be avoided by using a reflective back contact. We also demonstrate the possibility to reach a short-circuit current of $J_{sc} = 36.3 \text{ mA/cm}^2$ for a 150-nm-thick CIGS absorber with a silver nanostructured mirror. Preliminary results of nanostructured back contacts fabricated by nanoinprint lithography will also be presented.


ES20.07.11

Localization and Characterization of Secondary Phases in CIGS Thin-Film Solar Cells

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Secondary phases in Cu(In,Ga)Se$_2$ based thin film solar cells were found at the backside of the absorber layer in contact to the back contact. Such buried secondary phases are difficult to detect, but might influence the solar cell performance. Therefore, it is desirable to develop a methodology to localize and investigate them in detail. The CIGS layer was fabricated in a co-evaporation process under special conditions. Localization and further investigations can be done by removing the absorber from the back contact or by cleaving the sample with a focused ion beam or cross-section scanning electron microscope. Energy dispersive X-ray spectroscopy (EDS) measurements reveal a varying composition of the absorber elements. However, the forced detachment of the back contact from the absorber destroys the solar cell stack and might influence the appearance of the secondary phase itself. Furthermore, investigations of the solar cell stack as a whole are no longer possible. To overcome these problems, we electrically contacted a complete solar cell inside an electron microscope and used electron-beam-induced current (EBIC) to locate buried secondary phases. In EBIC images, the secondary phases show a reduction of the current density depending on the size and the morphology of the secondary phase. Hence, the reduction of the electron-beam-induced current allows the localization of secondary phases in a reliable way without destroying the solar cell. For verification and further investigations, we prepared thin cross section lamellas via focused ion beam at the localized buried phases. Several thin lamellas of the complete solar cell stack, including the underlying substrate, were investigated via EDS with a high spatial resolution of tens of nanometers revealing compositional variations.

ES20.07.12

(Ag,Cu)(In,Ga)Se$_2$ Thin-Film Solar Cells Analyzed by Atom Probe Tomography

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The incorporation of Ag in Cu(In,Ga)Se$_2$ (CIGSe) is understood to induce certain improvements in the opto-electronic properties of the absorber, which is reflected in enhanced conversion efficiencies [1]. Ag atoms substitute for Cu forming a pentanary (Ag$_x$Cu$_{1-x}$In$_y$Ga$_{3-y}$Se$_2$ (ACIGSe) alloy with a wider band gap compared to CIGSe absorber. The Ag alloying also allows to reduce the deposition temperatures due to the lower melting point of Ag, which as a result decreases the density of lattice defects in the absorber. Synthesizing such alloy on high strain K-rich substrates along with KF post deposition treatment displays higher device performance compared to similarly processed CIGSe devices without Ag [2]. The diffusion of alkali metals from the substrate in ACIGSe compared to CIGSe as well as the distribution of Ag in the absorbers are matters that can elucidate differences in the opto-electronic properties and therefore requires further attention.

Amongst various analytical techniques, atom probe tomography (APT) is an extremely promising tool to characterize the chemical distribution in three dimensions with sub-nm resolution [3]. APT is used in the study here as a main tool to examine local compositions within ACIGSe and the distribution of alkali metals within absorbers grown on different substrates; soda lime glass (Na-rich) and high strain point glass (K-rich), respectively. Na and K were found to segregate to different lattice defects in the absorber structures. Correlative measurements using transmission Kikuchi diffraction and APT were therefore carried out to investigate the crystallographic and chemical nature of grain boundaries and twin boundaries detected within the ACIGSe structures. Although ACGSe is a promising system for thin film solar cell technology, more research is certainly required to demonstrate if the beneficial effects observed for Ag additions are worth to pay for, considering its higher cost compared to Cu.


ES20.07.13

Studying the Light-Soaking Effect on the Absorber Layer of Cu(In,Ga)Se$_2$ Solar Cells Using Raman Analysis

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Culn$_{1-x}$Ga$_x$Se$_2$ (CIGS) is a promising absorber material for high-efficiency, low-cost thin-film photovoltaics, with a significant increase in efficiency in the last 3 years. To further improve the device performance, a better understanding of the absorber layer defects is required. One puzzling behavior is the effect of light soaking (LS). CIGS solar cells exhibit metastable performance under extended duration light illumination. This has been proposed to be related to amphoteric behavior of (V$_{Ga}^{2+}$/V$_{Ga}^{3+}$) vacancies; under light illumination, the equilibrium distribution of the donor and acceptor configuration of these vacancies changes. However, this hasn’t been shown experimentally [1]. Here, we report on metastable effects using Raman analysis during light soaking. Commercial Ag-alloyed Culn$_{1-x}$Ga$_x$Se$_2$ (ACIGS) sputter-deposited samples coated with CdS, were obtained from MiaSoLe HiTech. The samples were fabricated in a production-scale roll-coater on flexible stainless-steel substrates. Na and K alkali metals were incorporated from the Mo back electrode. Current-voltage analysis of the samples under the light soaking, dark heat, and combinations of both were measured at MiaSoLe. Raman spectra were measured every 1-2 minutes over a total time of 200 minutes using continuous 532 nm laser illumination. The sample temperature was maintained at 12°C by a Peltier device mounted under the sample. The excitation depth at this wavelength is ~100nm. The laser power was set at the lowest level at which reliable data could be obtained to prevent peak shifts due to local heating. Higher laser powers produced different but variable results. The results showed time-dependent variation in the A1 (CIGS) mode at 176 cm$^{-1}$. In addition, a broad shoulder related to the ordered defect compounds such as Cu(In$_{1-x}$Ga$_x$)$_2$Se$_2$ was detected at ~155 cm$^{-1}$. After 60 min illumination, the intensity of the CIGS A1 mode dropped while the ordered defect structure peak grew. For relatively stable samples, the A1/ODC stabilized at higher values after 200 min exposure; however, unstable samples stabilized at lower ratios. This suggests re-ordering of Cu-Se bonds under illumination. We are planning to study these effects as a function of temperature to establish the kinetic rate parameters of the changes.


ES20.07.14

In-Depth Analysis of Phase Distribution in Zn(O,S) Thin Films Deposited by a Reactive Sputtering

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Zn-based materials such as ZnO, ZnS, or Zn(O,S) are being widely used for optoelectronic devices, thin film transistors, and photovoltaic devices due to their wide bandgap, chemical stability, inexpensiveness, and nontoxicity. ZnO$_{1-x}$S$_x$ films especially show very interesting changes in electronic properties when the sulfur-to-oxygen composition ratio (x) is varied. With increasing x between 0 < x < 0.5, the conduction band minimum (CBM) hardly changes and the valence band maximum (VBM) moves up, while for x larger than 0.5, it is the CBM that moves up and the VBM remains nearly unchanged, which yields the bandgap bowing. A deposition method is an important issue to consider in the fabrication of the Zn(O,S) thin films with high quality, composition controllability, and industrial applicability. Among various methods of Zn(O,S) deposition, reactive sputtering is an attractive choice because it is manufacturing-friendly. However, a highly energetic plasma during the sputtering is likely to make undesired effects especially when forming very thin films.

In this study, the Zn(O,S) thin films were prepared using a single Zn target and O$_2$/Ar mixture gas. Despite careful control of the sulfur-to-oxygen composition ratio and its
gradient through the vertical direction, we found that the sulfur-to-oxygen composition ratio changed along the depth direction; the bottom layers became O-rich. Additionally, Zn(OH)2 secondary phase was observed at the bottom side of the Zn(O,S) thin films, which induced much lower VBM. The properties of the fabricated thin films and solar devices were characterized by a transmission electron microscopy, an energy dispersive spectroscopy, an X-ray photoelectron spectroscopy, and a current-voltage measurement. In this work, we present several strategies to mitigate the unwanted compositional variations and the formation of secondary phases to achieve high quality Zn(O,S) thin films with reactive sputtering. The details of these strategies will be presented. 

ES20.07.15
The Overall Distribution of Rubidium and Cesium in Highly Efficient Cu(In,Ga)Se2 Solar Cells Philip Schöppel1, Sven Schönher1, Philip Jackson2, Roland Wuerz2, Wolfgang Wisniewski1, Torsten Schwarz1, Maurizio Ritzer1, Andreas Johannes1, Maximilian Zapf1, Gema Martínez-Criado1,6, Claudia S. Schnoor1 and Carsten Ronning1,2.1 Institute of Solid State Physics, Friedrich Schiller University Jena, Jena, Germany; 2Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Stuttgart, Germany; 3Otto Schott Institute of Materials Research, Friedrich-Schiller-University Jena, Jena, Germany; 4Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany; 5European Synchrotron Radiation Facility, Grenoble, France; 6Instituto de Ciencia de Materiales de Madrid, Madrid, Spain.

Thin film solar cells based on the absorber material Cu(In,Ga)Se2 have achieved conversion efficiencies well over 22%. The recent push in record efficiencies was mainly realized by applying an alkali fluoride post deposition treatment (PDT) to the absorber. Best results were obtained for heavy alkali elements like Rb and Cs. In order to study the beneficial effect of the heavy alkali elements we investigated highly efficient Cu(In,Ga)Se2 solar cells, whose absorbers were subjected to either a RbF-PDT or a CsF-PDT. Thin cross sectional lamellas were cut out of the entire devices and analyzed via a combination of synchrotron based spatially resolved X-ray fluorescence analysis and different electron microscopy techniques. It is evident that Rb accumulates at random high-angle grain boundaries, at the p-n junction, and at the interface between the absorber and MoSe2 layer. The agglomeration of Rb at the grain boundaries is accompanied by a reduced Cu concentration and slightly increased In and Se concentrations. Furthermore, variations in the local composition of the absorber at the p-n junction indicate the formation of a secondary phase, which shows a laterally inhomogeneous distribution. In case of the CsF-PDT, we obtained similar results. Hence, the improved solar cell performance due to heavy alkali fluoride PDT can be expected to originate from a favorable modification of the p-n junction, the random high-angle grain boundaries or the back contact interface or from a combination of these effects.

ES20.07.16
Microstructure Alternation in Heterojunction Interface Engineering of CZTS Solar Cell Jiahong Huang, Kaiwen Sun, Xin Cui, Chang Yan, Martin Green and Xiaojing Hao; University of New South Wales, Sydney, New South Wales, Australia.

Kesterite Cu2ZnSnS4 (CZTS) photovoltaics have been comprehensively investigated in the past decades but are still hampered by a relatively large open circuit voltage (Voc) deficit, which is due to the non-radiative recombination within the CZTS bulk and hetero-interface region. Heterojunction interface engineering is of great importance to tackling the interface recombination problem by optimizing the band alignment between the absorber and the buffer and interface passivation. In this work, we reported a detailed characterization of the microstructure at the interface of the CZTS device with three different buffer materials using high-resolution TEM technique. It has been revealed that an ultra-thin ZnS or Zn (S, O) nanolayer can be formed at the CZTS and the buffer for the subsequent growth of ZnSnO and CZnS layers, while such feature has not been observed in the CdS buffer sample. Such ultra-thin ZnS or Zn (S, O) is found grown epitaxially at the CZTS surface with high crystallinity as the lattice mismatch between ZnS and the kesterite CZTS is negligibly small. The presence of this nano-structure between the buffer and CZTS absorber may benefit the device performance by reducing interface crystalline defects and thereby decrease the interface recombination while acting as a tunneling layer for current transport.

ES20.07.17
Crystal Structure of (In,Ga)Se2 Solid Solution Studied by XAFS Kosuke Beppu, Tetsushi Maeda and Takahiro Wada; Ryukoku University, Otsu, Japan.

Crystal structure of (In,Ga)Se2 precursor material was studied by X-ray absorption fine structure (XAFS) in order to prepare highly efficient Cu(In,Ga)Se2 (CIGS) solar cells. On the basis of the results, preparation process of high-quality CIGS thin films is discussed. The CIGS thin films were prepared by a 3-stage process. In the first stage, the initial stage consists of deposition of an (In,Ga)-Se precursor layer. In the second stage, the precursor layer is exposed to Cu and Se fluxes to form Cu-rich CIGS. In the third stage, In, Ga, and Se are added to the Cu-rich CIGS layer in order to obtain a slightly (In,Ga)-rich CIGS film. Then, the property for the first layer of (In,Ga)Se2 can affect the quality and crystal orientation of CIGS, which is finally obtained in 3-stage process. The crystal structure of InSe is hexagonal layered defect wurtzite type structure. The crystal structure of GaSe is monoclinic defect sphalerite type structure. Therefore, the crystal structure of (In,Ga)Se2 is predicted to be affected by a Ga content. In this work, we synthesized (In,Ga)Se2 and clarified their crystal structures. (In,Ga)Se2 was prepared by a mechanical method. (In,Ga)Se2 was characterized by X-ray diffraction (XRD) and XAFS. The XRD patterns of (In,Ga)Se2 were gradually changed with Ga content. The Rietveld analysis for the XRD patterns clarified the crystal structure of (In,Ga)Se2. When Ga content was more than 50 mol%, the layered defect wurtzite type structure can be obtained. When Ga content was more than 50 mol%, the layered defect wurtzite type structure can be obtained. The transition probability also showed change of the crystal structure of (In,Ga)Se2. Since an electron was easy to flow into the anti-bonding orbital due to the change of the crystal structure, the bond length varied and lattice parameter was changed.

ES20.07.18
Characterization of Defect Levels in BaSi: by DLTS and Significant Improvement of Photoreponsivity by Increasing Growth Temperature Yudai Yamashita, Takuma Satoh, Kaoru Toko and Takashii Suemasu; University of Tsukuba, Tsukuba, Japan.

Barium disilicide (BaSi2) shows great promise as a new material for thin-film solar cells. It has a suitable bandgap of 1.3 eV, large optical absorption coefficients exceeding those of CIGS,1,2 and a large minority-carrier diffusion length of about 10 µm.3,4 We achieved a conversion efficiency of 9.9% in p-BaSi2/n-Si heterojunction solar cells.3,4 We target next BaSi2 pn homojunction solar cells. To this end, high-quality BaSi2 light absorbers with low defect density (N D) are inevitable. In this work, we investigated defect levels and their values of V T in the BaSi2 layers by deep level transient spectroscopy (DLTS), and succeeded in reducing defects in BaSi2 films. In the first experiment, undoped BaSi2 absorber layers by DLTS. After thermal cleaning (TC) under UHV at 800°C, we grew a 500-nm-thick undoped BaSi2 layer by MBE using an optimized Ba/Si ratio on n-Si (111) (1×1014 cm-2) to form a heterojunction diode. The electron concentration (n) of the BaSi2 was below 1015 cm-3. The Schottky barrier height was 2×103 eV cm-3 at RT. The depletion region stretches in both sides. However, the defects on the Si substrate decrease to a value below the detection limit.4 For this reason, the detected peaks indicate defects in BaSi2. An upward facing peak caused by majority-carrier (hole) trap level (H1) was observed at approximately 126 K. The hole trap level was calculated to be approximately 0.27 eV from the valence band maximum, and N D was 1×1012 cm-3. This value is approximately 100 times smaller than that reported 5. As the DLTS signal near 125 K decreased as |R/|S| decreased and hence it approached the BaSi2/Si interface. This result shows detected defects existed in BaSi2, and their density decreased around the interface. When we changed the number of injected carriers by changing the pulse width (τp), the DLTS signal increased sharply as the τp increased from 0.1 to 10 ms, indicating the presence of point defects. First-principles calculation has revealed that Si vacancy (V Si) is most likely to occur.6 One of the calculated defect levels due to V Si is in good agreement with H1. In order to understand why the density of V Si decreases in BaSi2 close to the heterointerface, RBS measurement was carried out. The depth profiles of Ba to Si atomic ratios showed that BaSi2 was in excess of Si around the interface. This result means that Si atoms diffuse into the BaSi2 layer from the Si substrate during MBE growth and fill the Si vacancies. From this result, it is expected that promoting Si diffusion from the substrate is effective for reducing the density of BaSi2 defects. In the second experiment, in order to promote the diffusion of Si atoms from the Si substrate, we raised the substrate temperature (Tsub) during MBE growth from 580 to 650°C. In this experiment, we varied the Ba to Si deposition rate ratio (R Ba/R Si) from 0.4 to 4.7. The photoreponsivity changed drastically depending on R Ba/R Si and reached a maximum of around 2.7 A/W at 1.55 eV under the bias voltage of −1 V applied between the top and bottom electrodes when the R Ba/R Si was around 1.2. This value is more than three times larger than that reported 7, suggesting that the density of V Si was significantly suppressed.
Reducing the thickness of Cu(In,Ga)Se₂ (CIGS) absorber layers has potential to decrease its cost significantly, but has drawbacks like incomplete absorption and increased back-contact recombination, both resulting in power conversion efficiency losses. One solution is to implement a rear surface passivation layer, which has potential to reduce rear surface recombination velocity and increase rear internal reflection [1]. Alumina (Al₂O₃) is such an ideal passivation layer, but unfortunately also acts as an electron and diffusion barrier layer, and thus prevents current flow and sodium (Na) diffusion. As is discussed below, our novel approach to generate point contact openings in this passivation layer overcomes both problems at once. The proposed method is to use sodium fluoride (NaF) on top of the Al₂O₃ passivation layer, which will generate contact openings during selenization. This applied approach is industrially viable, as compared to proven methods – e.g. using nanoparticles, e-beam or nano-imprint lithography – which are too expensive, time-consuming or not applicable for larger areas. D. Ledinek et al. previously proposed using a very thin layer of Al₂O₃ rear surface passivation in combination with NaF deposition to enhance the electrical characteristics of CIGS solar cells. In their study this surface passivation is claimed to allow tunneling [2]. In our study, we prove that point contacts have been generated in this Al₂O₃ surface passivation layer. Atomic layer deposition (ALD) was used to deposit very thin Al₂O₃ layers on molybdenum (Mo) rear contact, and NaF was deposited on these layers by spin coating. Thereafter CIGS layers (>500 nm thick) were grown by single stage co-evaporation at 550°C, followed by standard solar cell process described in [3]. To detect the contact openings in the passivation layers, scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) spectroscopy was applied. Glass/Mo/Al₂O₃/NaF characterization samples were used for this analysis, where the co-evaporation process was mimicked by using a selenization step. After the selenization, point openings in the thin Al₂O₃ passivation layers were determined by SEM, and supported by EDX measurement. To investigate the impact of Al₂O₃ thickness on passivation of the CIGS rear surface, time resolved photo-luminescence (TR-PL) measurements on finished absorber layers (capped with CdS) were used. According to these TR-PL results, a 6 nm thick passivation layer gave the highest free charge carrier lifetime and PL response in all sets of samples. This was confirmed in full solar cell devices, where a significant increase in power conversion efficiency, and gain in open-circuit voltage, current density and fill factor values was measured for the 6 nm Al₂O₃ rear passivated CIGS devices, as compared to unpassivated reference cells. Hence, it can be concluded that by using a simple, cost-effective and fast way, i.e. ALD for Al₂O₃ and spin coating for NaF, we succeeded to make point contact openings to passivate the back surface of ultra-thin CIGS solar cells. The ongoing work focuses on different aspects: (i) At present the point openings are still submicron size, now we try to make them nano-size. (ii) We also concentrate on controlling the density of the contact openings, e.g. by changing the temperature of ALD process or the molarity of NaF solution. (iii) This approach also enables us to investigate different metal oxides as passivation layers, such as H₂O₂ and TiO₂ in combination with the same contact opening approach. (iv) And finally, we are investigating this rear surface passivation approach for other absorber layer deposition/growth techniques, e.g. a 2-step sputtering + selenization method.

[1] Poncelet, O. et al. DOI: 10.1016/j.solener.2017.03.001
revealed a characteristic time scale of 200 – 260 ps for recombination. Hall effect and TRTS measurements revealed electron and hole mobilities in the range of 50 – 100 cm²/Vs and a majority carrier density of 9x10¹⁴ cm⁻³. These dynamics result in a characteristic minority carrier diffusion length of less than 200 nm, leading to incomplete carrier collection, as confirmed by a strongly decreasing external quantum efficiency at long wavelengths for a device prepared on the crystal.

Carrier dynamics and device performance strongly depend on cation composition. Near-stoichiometric compositions (Cu/(Zn+Sn) > 0.92 and Zn/Sn < 1.12) had much shorter carrier lifetimes of less than 20 ps, which lead to Jₑₑ = 16.2 mA/cm², Voc = 220 mV, and efficiency = 1.7%. Low carrier lifetime, which may be due to the high density of cluster defects related to Cu₉₋₁₀Sn₉₋₁₀ antisites, limits Jᵥ and Voc as well as efficiency. To reduce the defect concentration, Ag was used as a substitute for Cu since the covalent radius of Ag is approximately 15% larger than that of Cu and Zn. With Ag/(Ag+Cu) = 0.29, lifetime increased by more than an order of magnitude to 9 ns, with associated increase in diffusion length up to ~1 μm. Improved performance with Ag alloying had previously been observed for polycrystalline thin films, with improvements partially ascribed to larger grains and changes to the chemistry of the grain boundaries. However, the dramatically increased lifetime that we observe with Ag alloying in single crystals indicates that reductions in bulk defect densities are likely the dominant factor. Incorporating Ag into CZTSSe devices may lead to increased efficiencies. Our approach combining ultrafast spectroscopy and device measurements can lead to more detailed understanding of performance-limiting photophysical processes and can subsequently accelerate the development of even more efficient PVs.

ES20.07.22
Ultrafast Carrier Dynamics at Proton-Bombarded Cu(In,Ga)Se₂ Thin Films Measured by Optical Pump-Thz Probe Spectroscopy

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The photoexcited carrier dynamics in optoelectronic devices such as photovoltaic and thermoelectric devices is a major research topic over the past decades. Chalogenide-based Cu(In,Ga)Se₂ (CIGS) thin film has attracted considerable attention as a material for photovoltaic devices with high radiation tolerance in space environment. However, very little empirical work has been done until recently, related to the studies on radiation damage and photoexcited carrier dynamics with radiation exposure in CIGS thin film. In this paper, we carried out the irradiation of H⁺ ion beams with injection energy of 200 keV into CIGS thin film by varying the concentration of H⁺ ions beams dose from 10¹⁵/cm² to 10¹⁶/cm². To investigate the optical and electrical property, the carrier concentration and hall mobility were evaluated as a function of H⁺ ions beams dose. To study photoexcited carrier dynamics after ion beams bombardment, optical pump-Thz probe (OPTP) spectroscopy were measured, which is sensitive to behavior of free carriers within ultrashort time scales of ps. Contrary to pure CIGS thin film, the carrier lifetimes of ion beams-bombarded CIGS thin film were drastically decreased, which is directly related to the surface defect states induced by radiation damage. Moreover, carrier lifetimes varied with the concentration of H⁺ ions dose due to different settlements of ion beams along the depth direction into the CIGS film.

Based on carrier-recombination process, we introduce an interpretation of the photocarrier dynamics in terms of surface defect states existed in the ion beams-bombarded CIGS thin film as a function of H⁺ ion dose.

ES20.07.23
Understanding the Role of CdS/CdSe Bilayer Window in CdTe Solar Cells via Capacitance Spectroscopy

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Over the last decades, the significant increase in short circuit current density has been considered as one of the most important factors that led to the current record efficiency CdTe solar cells. The improvement of short circuit current density is mainly achieved by incorporating Se into CdTe. The impact of Se incorporation is commonly attributed to the optimal band alignment introduced by the formation of CdSeₓ₁₋ₓTeₙ alloy. However, other possible mechanisms that may lead to the enhanced device performance, including the changes in the carrier density profile, trap state distributions in bulk and at interfaces, and barrier heights are yet to be systematically investigated.

In this work, a series of electrical characterization measurements are carried out to explore the effects of incorporating a CdSe interlayer in CdTe solar cells. Temperature dependent current density-voltage (J-V-T) measurements are performed to extract the Shockley back barrier heights for devices with different CdSe and CdS cell thicknesses. Temperature dependent capacitance–voltage (C-V-T) measurements are used to compare the charge carrier density distributions through the absorber layers. In addition, thermal admittance and impedance spectroscopy measurements are carried out to explore the defects in bulk and at interfaces, conductivity, and carrier mobilities. Combining these advanced electrical characterization techniques allows us to probe the origins of the enhanced performance in CdSeₓ₁₋ₓTeₙ solar cells. Our study would supply a better understanding of Se incorporation in CdTe absorber layers, thus providing guidelines to further improvement of CdTe solar cells.

ES20.07.24
The Impact of Band Tails on Charge Carrier Dynamics and Solar Cells

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In many photovoltaic materials the impact of disorder and band tails is discussed controversially and it is unclear whether extended band states or localized tail states dominate charge carrier dynamics. Here, we investigate the effect of band tails on charge carrier transport and recombination and interpret it in a novel way and deduce the consequences for solar cells. To this end, we probe photoexcited charge carriers in a kesterite-semiconductor as a model system over their full life span from femtoseconds to microseconds by time-resolved terahertz spectroscopy and photoluminescence spectroscopy. We find that occupation of the band tails is strongly temperature-dependent. Above a characteristic temperature charge carrier are activated out of Urbach tail states. This mobility value is at least one order of magnitude lower than in a theoretical tail-free kesterite-semiconductor. Further, the mobility at terahertz frequencies indicates that charge carriers localize in tail states with a typical spatial extent of 11 nm. The recombination kinetics of photoexcited charge carriers can be described within the Shockley-Read-Hall model of defect assisted recombination. Unambiguous signs of an influence of band tails are not measured at room temperature, but secondary effects from the affected carrier distribution and transport are discussed. The non-radiative recombination is found to be the major bottleneck for a potential solar cell and reduces the open circuit voltage of a potential solar cell by 270 mV. However, below the characteristic temperature of 200 K charge carrier relax by multiple-trapping into the deep Urbach tail and lead to a strongly injection-dependent charge carrier distribution, transport and recombination as previously observed for amorphous semiconductors.

ES20.07.25
Voltage Loss Analysis for CZTSSe Solar Cells with Sn Content Variation

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The absence of toxic and scarce elements makes kesterite (Cu(In,Ga)Se₂) a promising inorganic thin film photovoltaic technology, but its performance advancement is hindered by a substantial voltage loss. This is commonly expressed as the open circuit voltage deficit (ΔVoc,deficit = Voc – Vocₐₚ) which requires bandgap determination. The band tails that characterize kesterite absorption spectrum make bandgap evaluation inaccurate and dependent on the method, thus Voc-deficit interpretation is unreliable for proper performance comparison. It was demonstrated by Yao et al. (Phys. Rev. Appl., 4, 1 (2015)) that from the reciprocity principle and the external quantum efficiency it is possible to measure voltage losses avoiding the bandgap estimation.
of 27 at%, Voc and V_{oc,real} were the lowest of the series whereas electroluminescence quantum yield (QE_{LED}) was the highest (5.2×10^-4 %). This indicates that the lowest photovoltaic performance does not always correlate with a high non-radiative recombination in kesterite solar cells. This is also supported by temperature dependent current-density (JV-T) and capacitance-frequency (CF-T) measurements confirming the Sn variation has no appreciable influence on the defect distribution.

It is concluded that QE_{LED} obtained by means of EL and EQE measurements is a suitable indicator of non-radiative losses for compositionally complex absorbers like kesterite.

ES20.07.26
Characterization of Thin CdTe Solar Cells with a CdSeTe Front Layer
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CdTe telluride (CdTe) photovoltaic device efficiencies show significant improvement with the incorporation of a cadmium selenium telluride (CdSeTe) alloy layer deposited between the magnesium zinc oxide (MgZnO) device emitter and CdTe absorber layers. CdSeTe/CdTe devices are fabricated by close-space sublimation with a total absorber thickness of 1.5 µm. At this thickness, both the CdSeTe and CdTe layers are fully depleted. The incorporation of the CdSeTe layer is confirmed by microscopy measurements and shows minimal grading of Se into the CdTe layer. Loss analysis calculated from optical measurements shows that the CdSeTe layer acts as the primary absorber in the CdSeTe/CdTe structure, absorbing at least 90% of the photons. Current density-voltage measurements show an increase in current density of up to 3 mA/cm² with the addition of a CdSeTe layer that is due to a band gap shift from approximately 1.5 to 1.43 eV for CdTe and CdSeTe/CdTe absorbers respectively, where band gaps are determined by quantum efficiency and spectral photoluminescence measurements. Improvement in CdSeTe/CdTe device quality compared to CdTe is reflected in spectral photoluminescence measurements which show peak intensities many times greater when Se is incorporated into the absorber. The voltage deficit, calculated as the difference between the optimal absorber band gap and the measured open circuit voltage, shows improvement with the incorporation of the CdSeTe layer. This is corroborated by improved electroluminescence intensity, which is proportional to voltage deficit. The incorporation of CdSeTe as part of the absorber layer in CdTe device structures improves device current density and voltage deficit and has therefore increased device efficiencies by 2% absolute for CdSeTe/CdTe absorbers with a total thickness less than two microns.

ES20.07.27
Flexible Cu(In,Ga)Se₂ Solar Cells for Outer Planetary Missions—Investigation Under Low Intensity Low Temperature Conditions
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Cu(In, Ga)Se₂ (CIGS) solar cells have been studied for space applications for a number of years due to their radiation tolerance and low cost. Most early work has studied CIGS on soda lime glass, which is too bulky for space applications, and would not allow for the complex folding arrays that have been proposed for future deep space missions. Here, commercially available flexible CIGS solar cells are investigated under conditions consistent with those around the outer planets. Performance under these low temperature low intensity (LILT) conditions is critical to study, as these conditions can reveal issues not present under normal operation [1]. Current density-voltage (J-V) and external quantum efficiency (EQE) measurements under different space conditions, illumination, and bias conditions are performed to investigate the environmental effects of these deep space conditions. Of particular interest at low temperature is the behavior of the well-known Ve-Vce metastable defect [2], and its potential role in device performance under LILT conditions. Here, evidence of a photo-activated barrier is observed, which is attributed to the same defect center, although its effect on power generation at LILT conditions appears to be minimal. Additionally, proton irradiation with high fluence levels is investigated to emulate certain conditions near Jupiter. Although degradation is observed, self-healing behavior under annealing conditions is also evident. [1] D. A. Scheiman and D. B. Snyder, “Low intensity low temperature (LILT) measurements of state-of-the-art triple junction solar cells for space missions,” in 2008 33rd IEEE Photovoltaic Specialists Conference, 2008, pp. 1-6. [2] S. Lany and A. Zunger, “Light- and bias-induced metastabilities in Cu(In,Ga)Se₂ based solar cells caused by the (Ve-Vce) vacancy complex,” Journal of Applied Physics, vol. 100, no. 11, p. 113725, 2006/12/01 2006.

ES20.07.28
Real Time Spectroscopic Ellipsometry Analysis of the Structural Evolution and Optical Properties of CuInSe₂ by One and Two Stage Thermal Co-Evaporation
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Real time spectroscopic ellipsometry (RTSE) measurements have been performed on copper indium diselenide (CuInSe₂) narrow bandgap solar cell materials. In these studies, thin film CuInSe₂ absorber structures have been deposited in one-stage and two-stage thermal co-evaporation processes on smooth c-Si wafer substrates held at temperatures in the range of 300-570 °C. Analysis of the RTSE data for one-stage CuInSe₂ yields the structural evolution and the complex dielectric functions (ε₁, ε₂) of the individual CuInSe₂ layers, the latter relevant for the elevated temperatures of deposition. In this analysis, information on the structural evolution, i.e. the surface roughness and underlying bulk layer thicknesses versus time, is obtained with monolayer-level sensitivity during thin film nucleation and coalescence. Complex dielectric functions (ε₁, ε₂) of deposited films as well as their bandgap energies and broadening parameters are obtained at different measurement temperatures applying the combination of RTSE and in situ SE measurements during sample cooling. All such deduced information on the structural and optical properties provides insights into CuInSe₂ film crystallinity and grain growth processes. In the two stage process, CuInSe₂ is obtained by depositing either In₃Se₄ or Cu₃Se₄ first, followed by exposure to either Cu₃Se₂ or In₃Se₄ evaporant, respectively. Real time SE has been applied to both stages of each CuInSe₂ deposition in order to compare the structural and optical property evolution characteristic of the two different routes for CuInSe₂ fabrication. The goal of this work is CuInSe₂ of optimum stoichiometry and grain structure obtained under RTSE monitoring and control for use as a bottom cell absorber material in tandem solar cell applications. Results correlating structural evolution and ultimate device performance will be reported.

ES20.07.29
Highly Efficient Earth-Abundant CZTSSe Solar Cell by Introducing p+-CTSSe Point Contacts
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Recently, Cu₂ZnSn(S,Se)₄ (CZTSSe) solar cell has attracted many attentions due to several advantages of CZTS(e) such as earth-abundant, cheap, nontoxic, high absorption coefficient (~10⁷ cm⁻¹) and tunable bandgap (1.15-1.5 eV). So far, the highest efficiency of CZTS(e) solar cell is 12.6% achieved by IBM team but its power conversion efficiency (PCE) still cannot compete with the commercial thin-film solar cells, e.g., CIGS and CdTe. There are numerous issues need to be solved to enhance the PCE (e.g., back contact losses, interfacial losses, deep defects). Especially, back contact losses cause degradation of CZTS(e) solar cell due to interface defects between CZTS(e) and MoO₃ layer [1]. The metallic precursors prior to CZTSSe sulfo-selenization, producing p+-CTSSe and ZnSe, which helps reduce interface recombination, on the bottom of the CZTSSe absorber layer. The main improvement results from increasing fill factor (FF) and short circuit current due to less recombination at back interfaces. Moreover, a 9.61% PCE (~10.6% in J-V) and Li-Chyong Chen

References
Effect of Combined Alkali (KF + CsF)-Post-Deposition Treatment on Cu(In,Ga)Se₂ Solar Cells

Ha Nguyen, Guy Brammertz, Chirila et. al. DOI: 10.1038/NMAT3789

We report a novel approach to generate plasmons in CIGSe thin films in the wide spectral range. In this work, a new methodology to generate plasmons in the CIGSe thin film used dual-ion beam sputtering. The valence band offset at n-type Mg₂Zn₁₋ₓSnₓO (MZ1) p-CIGSe heterojunction interface can be determined by the core-level photoemission-based method. Here, the calculation of was done by two methods: (1) considering different core level peaks of Se 3d and Mg 2p for CIGSe and MZ1, respectively, and (2) considering same core-level peaks of Zn 3d for CZTSSe and MZ1. The values of valence band onset (VBOn), as obtained by linear extrapolation of the onset of the valence band, are 2.97 and 0.54 eV, respectively. Figure 1(a) shows the core-level peaks of the MZ1/CZTSSe heterojunction. The core-level spectra of Zn 3d recorded on the MZ1/CZTSSe heterojunction is dominated by one symmetric peak, implying a uniform bonding state. Figure 1(b) shows transmission spectra using ellipsometry. Figure 1(c) shows the energy band diagram calculated using Ultra violet photoelectron spectroscopy (UPS).

CIGSe layers have recently set a new record efficiency of 22.9%, thus demonstrating a continuous improvement of this technology. Currently, the standard thickness for the CIGSe absorbers is 2-3 μm. Reduction in material consumption will help to further reduce the cost. When approaching the material reduction by reducing the absorber thickness to below 700 nm leads to increase in production quantity but, on the other hand, it considerably reduces light absorption in absorber layer causing in strongly enhanced recombination at the back contact. Here, we will focus on the optical aspect and investigate a novel means to generate broadband plasmonic generation in ultrathin CIGSe layers for enhanced absorption in solar cells.

We report a novel approach to generate plasmons in CIGSe thin films in the wide spectral range. In this work, a new methodology to generate plasmons in the CIGSe thin film used dual-ion beam sputtering (DIBS) system is reported. Sputtering of material during growth by utilizing secondary DC ion source present in the DIBS system leads to the generation of different metallic and metal oxide nanoclusters of its constituent elements. Moreover, the formation of nanoclusters and generation of plasmons are verified by electron energy loss spectra obtained by UPS analysis, FESEM, and spectroscopic ellipsometry. Additionally, calculation of valence bulk, valence surface, and particle plasmon resonance energies are performed, and indexing of each plasmon peaks with corresponding plasmon energy peak of the different nanoclusters are done. This approach offers a convenient method to produce plasmon resonance across the broad spectral range spanning 2.1-10.74 eV. Further, use of this dual ion beam sputter instigated plasmon enhanced absorbers can be a novel mean to enhance the performance of photovoltaic devices.

Alkali metal (Na, K, Rb, and Cs) incorporation or post-deposition treatment (PDT) is known to be effective in improving the conversion efficiency of Cu(In,Ga)Se₂ (CIGSe) and Cu(InGa)₅(S)₇Se₃-thin film solar cells. Among them, Cs has been known to boost Voc and Jsc in CIGSe, and the world-record cell is also based on this technique. A new world-record CIGSe efficiency of 22.9% has been achieved in the research cell of Solar Frontier K.K, by CsF-PDT. However, CsF-PDT effects have been rarely studied, and therefore, it is worth to investigate the Cs incorporation.

This study reveals CIGSe-post-deposition treatment (PDT) effects on a Cu(InGa)₅(S)₇Se₃ (CIGSe) cell in comparison with KF-PDT effects. After CIGSe growth, we performed three different alkali-PDTS (KF, CsF, and combined KF + CsF) on CIGSe thin films, and examined the material and cell properties. Both KF- and CsF-PDT CIGSe cells showed similar cell efficiency improvements (~17.5%) compared to the untreated CIGSe cell (~16%). However, the reasons for the improvement differed. The CIGSe cells with KF-PDT exhibited further reduction in the recombination at the CdS/buffer interface compared to the CsF-PDT CIGSe cell. On the other hand, the CIGSe cell with CsF-PDT exhibited further reduction in the recombination in bulk compared to the KF-PDT CIGSe cell. Therefore, the overall conversion efficiency (18.4%) due to cooperative alkali incorporation effects. This device exhibited reduced recombination at both the Cds/CIGSe interface in the space charge region (SCR) and bulk compared to all other cells. Finally, we achieved a highly efficient combined alkali-PDT CIGSe device (20.15%) by applying a MgF₂ anti-reflective coating layer.

The biggest difficulty for improving the power conversion efficiency of Cu₂ZnSn(S, Se)₄ (CZTSSe)CdS/ZnO thin film solar cells is improving the open circuit voltage (VOC). Probably leading causes of the VOC deficit in CZTSSe devices have been identified as bulk recombination, band tails, and the intertwined effects of CZTSSe/CdS band offset, interface defects, and interface recombination. In this work, we predicted the CdS buffer layer by Mg-doped ZnO (Mg₂Zn₁₋ₓSnₓO) and measure the interface of n-type Mg₂Zn₁₋ₓSnₓO (MZ1) p-CZTSSe heterojunction interface can be determined by the core-level photoemission-based method. Here, the calculation of was done by two methods: (1) considering different core level peaks of Se 3d and Mg 2p for CZTSSe and MZ1, respectively, and (2) considering same core-level peaks of Zn 3d for CZTSSe and MZ1. The values of valence band onset (VBOn), as obtained by linear extrapolation of the onset of the valence band, are 2.97 and 0.54 eV, respectively. Figure 1(a) shows the core-level peaks of the MZ1/CZTSSe heterojunction. The core-level spectra of Zn 3d recorded on the MZ1/CZTSSe heterojunction is dominated by one symmetric peak, implying a uniform bonding state. Figure 1(b) shows transmission spectra using ellipsometry. Figure 1(c) shows the energy band diagram calculated using Ultra violet photoelectron spectroscopy (UPS).
Correlated to linear behavior of I-V experimental curves as measured by four-point probe on MoS

Modeling Influence of Diffuseness on Real-Life Solar Module Performance

ES20.07.37

Improved for the sulphurised samples. The formation of stoichiometric CZTS is an important factor to use it as an absorber layer in a thin film solar cell. The Ultra-violet Cu, Zn, Sn, S in required ratio. The presence of O and C was also detected due to atmospheric contamination. It is evident from the atomic % calculation that the stoichiometry has their composition are discussed in this paper. The composition of the CZTS thin film samples were studied using X-ray photoelectron spectroscopy, which revealed the presence of Cu, Zn, Sn, S in required ratio. The presence of O and C was also detected due to atmospheric contamination. It is evident from the atomic % calculation that the stoichiometry has improved for the sulphurised samples. The formation of stoichiometric CZTS is an important factor to use it as an absorber layer in a thin film solar cell. The Ultra-violet photoelectron spectroscopy was used to study the ionization energy, electron affinity, electronic band gap of the material and the data were in relation to reported results. Thus, from the XPS results it is obvious that the sulphurised CZTS thin films can be used as absorber layer in a thin film solar cell.

ES20.07.36

On the Electronic Structure of SiO$_2$/Mo$_2$ Interface by Density Functional Theory

ES20.07.35

We performed density functional theory calculations using CASTEP algorithm to understand the electronic structure of MoS$_2$ layers as most geometrical stable and pertaining of density of states for d-orbital from semiconducting into a semi-metallic was found and it could be correlated to linear behavior of I-V experimental curves as measured by four-point probe on MoS$_2$/SiO$_2$ thin films (~100nm).

ES20.07.37

Modeling Influence of Diffuseness on Real-Life Solar Module Performance

In this work, we investigate the effects of heat, light and voltage bias on the metastable behavior of CIGS solar cells through accelerated stress tests (AST) on the order of days (50 - 100 hours) in influence to the thin-film PV stabilization tests in IEC 61215-2 standards. A comprehensive analysis of devices with different alkali treatments using current-voltage (I-V), capacitance-voltage (C-V), quantum efficiency (QE), time-resolved photoluminescence (TRPL), and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to propose a preliminary mechanism for changes in device parameters with AST. Additionally, in-situ I-V characterization has been used to determine activation energies of change in $V_{oc}$ to further understand the effect of Na incorporation on the underlying mechanisms.

Three sample types were prepared at ZSW for accelerated stress testing: Type A with baseline Na, Type B with intended reduced Na with the introduction of a sputtered AlO$_x$-AlN barrier to reduce Na diffusion from the substrate and Type C with baseline Na plus a RbF post-deposition treatment. The CIGS layer was deposited by coevaporation process and the CdS buffer layer was deposited by chemical bath deposition (CBD) according to standard procedures. The buffer-window stack for Types A, B and C samples was CBD CdS followed by sputtered undoped ZnO and Al-doped ZnO layers. The cells were completed with Ni/AlNi grid contacts and the cell separation was done by mechanical scribing. Three primary stress factors considered in this study are voltage (low and high internal field), illumination (light and dark), and temperature (room temperature to 85°C). Under illumination and open-circuit (OC) conditions, the photogenerated charge carriers must recombine entirely internally, resulting in a decrease in built-in field. However, under short-
A conversion efficiency up to 20% have been recently achieved on the thin film cells using epitaxial Cu(In,Ga)Se$_2$ epi-CIGSe absorbers [1]. This high performance, large domain size and surface smoothness make the epi-CIGSe one of the excellent platforms to investigate electronic structure and effect of post deposition treatment (PDT) on it. In this study, we have studied surface potential, surface photovoltage over epi-CIGSe, band alignment at CdS/epi-CIGSe interface and effect of PF-KPT on them by Kelvin probe force microscopy, and photoemission and inverse photoemission spectroscopy.

Epi-CIGSe absorbers composed of Cu$_{n}$(In$_{0.6}$Ga$_{0.4}$Se$_{2}$ bottom- and Cu$_{n}$In$_{1-x}$Ga$_{x}$Se$_{2}$ top-layer grown on GaAs (001) substrate by molecular beam epitaxy were used as specimens. The cells using epi-CIGSe absorber and ZnO window layer of deposition of ZnO and light soaking showed a conversion efficiency of 20%. Details of preparation conditions were shown in the previous paper [1]. Surface photovoltage was determined from surface potential change induced by illumination of 685 nm light with an intensity about 10 mW/cm$^2$. CdS buffer was deposited onto the epi-CIGSe by $in$-situ evaporation. All of the measurements were performed at a pressure of low 10$^{-5}$ Pa scale.

AFM measurements reveal that surfaces of the epi-CIGSe consist of wide and atomically flat terraces and ridges with a height below few tens nm. The latter is parallel to anti-phase domain boundaries along [1 1 0] direction of the chalcopyrite phase. It is noteworthy that any edges of crystalline facets are hardly observed. Surface potential of the polycrystalline CIGSe films consists of two components and the width of each component is about 120 mV. These features are attributed to variations in crystalline planes and in surface terminations over poly-CIGSe. KF-PDT selectively suppressed the higher voltage-side component that should be attributed to anion-termination dominant facets. For the polycrystalline CIGSe films consists of two components and the width of each component is about 120 mV. These features are attributed to variations in crystalline planes and in surface terminations over poly-CIGSe. KF-PDT selectively suppressed the higher voltage-side component that should be attributed to anion-termination dominant facets.
Among the alternatives for CdS buffer layers in Cu(In,Ga)Se₂ oxidation-/reduction cycles and their reversible effect on the dipole formation on chalcopyrite surfaces, sometimes even above, CIGSe devices with a chemical bath-deposited (CBD) CdS buffer layer. Additionally, increasing the Ga/(Ga+In) (GGI) ratio allows increasing the bulk.

To evaluate the band alignment of CdS/CZTGe heterointerface, n-typed CdS buffer was deposited onto the CZTGe by thermal evaporation technique. He(I,2s) and Al(Ka) lines were used as the light source in the UPS measurements. All the bands of the CBD, UPS, IPS, and CDS depositions were performed in ultra-high vacuum condition (pressure < 10⁻⁷ Pa) without air exposure.

The UPS and IPS reveal the Fermi-levels are located near the center of the bandgap of CZTGe with x from 0 to 1. Although this hole concentration is much smaller than that (~10¹⁸ cm⁻³) in the CZTGe bulk, laser-irradiated XPS revealed that the origin of the hole deficiency near the surface is due to defects distributed closer to CZTGe surface than in the bulk, rather than Fermi-level pinning at the CZTGe surface. Moreover, we determined the conduction and valence band offset (CBO and VBO) at the CdS/CZTGe heterointerface relative to Ge composition x by using XPS, UPS, and IPS measurements by stepwise CdS deposition (e.g. CdS film thickness = 0, 3, 6, 30 nm). The CBOs decreased from -0.36 to -0.01 with increasing of x. A positive CBO indicates that the position of the conduction band minimum (CBM) of the CdS is higher than that of CZTGe, which is so-called “spike” conduction band alignment whereas the band alignment is flat in x = 1. In contrast, the VBOs remain constant and are around 1.1 eV. We revealed these CBO and VBO relative to Ge composition can be explained by the theoretical calculation. In the case of high performance CIGS heterojunction solar cells, the CBO at the Cds/CIGS heterointerface have CBOs from 0 to ~0.30 eV. Concerning it, we conclude CBOs at the CdS/CZTGe heterointerface with x from 0 to 1 are significant adequate value for the high performance solar cells in a point of electronic structure at the interface. Despite of it, cell performances of our CdS/CZTGe heterojunction solar cells drastically decreased with increasing of x over 0.2. We will discuss the relationship between band alignment of CdS/CZTGe and solar cell performances.

Among the alternatives for CdS buffer layers in Cu(In,Ga)Se₂ (CIGS)-based thin-film solar cells, In₅S₃ is a very promising candidate, leading to cell efficiencies very close to, or sometimes even above, CIGS devices with a chemical bath-deposited (CBD) CdS buffer layer. Additionally, increasing the Ga/(Ga+In) (GGI) ratio allows increasing the bulk band gap of the absorber, which in turn is expected to lead to higher open-circuit voltages. To optimize the design for both, GGI ratio and alternative buffer layer, an important prerequisite is a detailed knowledge of the electronic and chemical structure of CIGS absorber surfaces with varying GGI ratios, their interfaces with CBD-In₅S₃ buffer layers, and the chemical and electronic properties of the final film (i.e., full-thickness buffer layer). In this contribution, laboratory-based photoelectron spectroscopies (XPS, UPS, IPS), x-ray excited Auger electron spectroscopy (XAES), as well as synchrotron-based soft-x-ray emission spectroscopy (XES) are used to acquire this information. With these complementary spectroscopic methods, important insights into, e.g., elementary ratios at the surface of the investigated absorbers, intermixing processes at the interface, buffer layer growth properties, and characteristic species in the buffer layer, are gained. The results of these measurements allow us to discuss the chemical and electronic structure of the CIGS-In₅S₃/CIGS interface for different GGI’s.

An assessment of the intrinsic electronic properties of chalcopyrite surfaces is crucial to understand the characteristics of the window/absorber interface and related post-deposition treatments in chalcopyrite solar cells. However, a basic understanding of the involved processes is complicated by surface oxidation, granular inhomogeneities and grain boundaries. To gain access to the fundamental electronic properties of chalcopyrite surfaces, we focus on epitaxially grown CdSe₅S₃ (epi-CISe), which forms the energetically most favorable {112} facets upon slight Cu depletion. Scanning tunnel spectroscopy (STS) is a valuable tool in assessing whether chalcopyrite surfaces are electronically defective or passivated. Here, we carry out STS measurements on epi-CISe surfaces along with complementary surface-sensitive techniques such as X-ray, ultraviolet and inverse photoelectron spectroscopies (UPS/IPS/IPS). In this way, the local defect density is correlated with the energy level alignment and dipole effects at the surface upon various annealing and wet-chemical treatments relevant for device fabrication.

We compare the initial (as-grown) condition of epi-CISe samples (without any air exposure) to the states after oxidation in air, etching in NH₃ or KCN, as well as subsequent annealing in ultra-high vacuum (UHV). In the as-grown condition, the sample surface is found to be intrinsically passivated with a low defect level density. Based on this, a consistent determination of the surface band gap by STS and UPS/IPES reveals a value of 1.65 eV in accordance with density functional theory calculations reported earlier. Furthermore, our measurements provide evidence for the absence of any local or global surface dipole(s). These findings are in line with previous theoretical models predicting that the intrinsic dipole(s) of the polar facets in CISe are compensated by shallow surface defects. Nevertheless, our STS data do not show any spectral signatures of the corresponding defect levels, possibly due to their shallow nature. In contrast, upon oxidation in air, an overall high surface defect level density in conjunction with a considerable net-surface dipole associated with a potential drop of ~0.7 eV at the surface is observed. This surface dipole is accompanied by an upward band bending that shifts the surface Fermi level position from mid-gap (for the as-grown state) to p-type conditions. The high defect level density together with the dipole layer and the upward band bending persist even after removal of the surface oxides by wet-chemical NH₃ or KCN etching. Yet, a subsequent annealing in UHV restores the initial sample condition, as concluded from the absence of surface dipoles and passivation of surface defect levels. Our results shed new light on previous reports on lateral inhomogeneities on polycrystalline chalcopyrite surfaces, emphasizing the relevance of oxidation-induced dipole effects on chalcopyrite surfaces for the window/absorber interface design in chalcopyrite solar cells.


10:00 AM BREAK
CIGS solar cells are known to exhibit strong metastable behaviour and, in consequence, lot of experiments do not follow textbook interpretations. To name only two most basic measurements - light current voltage characteristics, and hence the parameters which determine the efficiency, as well as free carrier concentrations revealed by capacitance profiling, depend very strongly on the direction of the voltage sweep and/or the history of the sample. Therefore, sooner or later, everyone dealing with electro-optical characterization of CIGS solar cells experiences a kind of frustration, and metastable behaviour is often seen as an obstacle to understanding and progress. In this presentation we will show that, if analyzed with care, metastabilities can also serve as a valuable tool for investigation of CIGS-based devices. We will begin with a proposition of new classification of metastabilities. Then, we will critically review the theoretical models proposed to explain some of the observed phenomena with a special emphasis on their importance for the interpretation of experimental results. Finally, we will present how the analysis of metastable behaviour can shed some light on the role of sodium, potassium, and the deposition of different buffer layers.

11:00 AM ES20.09.02
Analysis of Recombination as a Function of Depth in Cu(In,Ga)(S,Se)2 Solar Cells
Alban Lafuente-Sampaio1, Jingdong Chen1, Shenghao Wang1, Mohamed M. Islam1, Takuya Kato1, Hiroki Sugimoto2, Katsuhito Akimoto3 and Takeaki Sakurai1; 1University of Tsukuba, Tsukuba, Japan; 2Solar Frontier, Tokyo, Japan.

A world record for Cu(In,Ga)(S,Se)2 (CIGS) efficiency of 22.9% has been achieved recently by Solar Frontier K.K. using Cesium treatment (Cs treatment). A common explanation for the high efficiency of the cells after alkali metal treatment is that processing passivates defects at the p-type CIGS absorber surface or grain boundaries. It is also known that the high performances of CIGS treated with alkali metal are linked to an increase of the open circuit voltage (VOC) [1]. However, the underlying physics of this effect has yet to be fully understood. To analyse the recombination mechanisms, we investigated the open current voltage at different excitation wavelengths and intensities of CIGS solar cells treated with potassium treatment (K-treatment). Based on the dependence of the CIGS Se absorption coefficient with wavelength, low energy radiation will penetrate deeper in the alloy than high energy one. Thus, the variations in wavelength and intensity open the possibility to study the recombination at different depths in the cells. Looking at VOC evolution, we can deduce the recombination rate of the CIGSSe as a function of the depth. The results of such experiment show that the untreated samples VOC decreased with excitation intensity and presents a dependence with the excitation wavelength, while the K treated samples does not have such a behaviour. This evidence a defect level in the absorber of the untreated sample which obstruct the collection of the carriers in the bulk. Using UCSAP-1D device modelling software, with a double grading structure, we investigated the recombination rate in the solar cell as a function of the depth. We evidence two different regions of recombination, in the bulk and in the depletion region. We show that the amount of recombination in each of the region depends both on the excitation wavelength as well as on the excitation intensity. The simulation was also done for different defect density, which shows that for a low defect density, recombination occurs only in the bulk, while for high defect density, recombination also occurs in the depletion layer. This creates a loss for the carrier collection, reducing the solar cell efficiency. The increase of the VOC in K-treated sample is then well explained by suppressing defect levels in the absorber layer.


11:15 AM ES20.09.03
Phonon Coupling and Shallow Defects in CuInS2
Alberto Lomuscio, Mohit Sood, Michele Melchiorre and Susanne Siebentritt; University of Luxembourg, Belvaux, Luxembourg.

Copper indium gallium disulfide Cu(In,Ga)S2 or CIGS is a promising absorber material for thin film solar cells due to its direct band gap energy that can be tuned from 1.5 eV (pure CIS) to 2.4 eV (pure CGS). It is suitable to make single- and multi-junction solar cells. In fact, it could be used as top cell in a tandem configuration with Si or CIGSe as bottom cell. However, Cu(In,Ga)S2-based solar cells still suffer from a low efficiency compared to their counterpart Cu(In,Ga)Se2-based solar cells, that have reached a record conversion efficiency of 22.9%. This is mainly due to a low open circuit voltage. Recently, a new fundamental breakthrough came when Hiroi et al. reached the world record efficiency of 15.5% with pure sulfide CIGS solar cell[1] and open circuit voltage up to 973 mV, using processing temperatures above those used traditionally (~550°C). Nevertheless, there is a lack of knowledge regarding the recombination processes and intrinsic defects for this chalcopyrite material. In fact, a deeper understanding is needed to better control the electronic properties, therefore to further improve the performance of devices based on this absorber material.

In this work, we present a detailed photoluminescence (PL) investigation of polycrystalline CIS thin film and we compare the results to those reported in literature. The sulfide CIS absorbers were deposited on molybdenum coated soda lime glass in a PVD system under copper excess (Cu-rich) in a single stage coevaporation using a deposition temperature of 650 °C. The secondary phase CuS was removed by KCN etching, reaching a Cu over In ratio of 1. The low temperature PL measurements were carried out with a 663 nm wavelength laser as excitation source using a liquid Helium flow cryostat. Moreover, temperature dependent admittance measurement (ADM) were carried out on both finished devices and aluminium coated absorbers to form a Schottky contact. The PL spectra recorded at 10 K are dominated by excitonic luminescence together with defect related peaks at 1.39 eV, 1.35 eV, 1.31 eV and 1.27 eV. The excitation dependent measurements over seven order of magnitude revealed that the 1.39 eV is a donor-acceptor transition (DA) with an energy shift of the peak position of 3 meV/decade. The same shift has been found for the other transitions at lower energy. The three peaks at 1.35 eV, 1.31 eV and 1.27 eV well match the Poison distribution as phonon replica of the main peak (1.39 eV) with a Huang-Rhys factor of 0.45 and a phonon energy of about 40 meV. We therefore attribute this series of peaks to a DA transition with its phonon replica. In order to get the energy position of the defects involved in the DA transition, temperature dependent PL has been performed. We found that at 90 K the luminescence clearly becomes a free to bound transition (FB), with the shallower defect ionized. From its peak position, we extracted a defect energy of 140 meV. This value is in good agreement with the activation energy of the main step of the capacitance measurements on both devices and Schottky contact.

We do show that the 140 meV defect is a bulk defect and not an interface defect as reported in some previous works. In addition, we attribute the 1.35 eV peak to the first phonon replica of the main DA transition, together with second and third one clearly visible. This is in contradiction with previous reported studies that generally explain the 1.35 eV transition as DA with a deeper donor involved, because the further phonon replica could not be detected.

maximum achievable $V_{OC}$ that a semiconductor can generate in a solar cell and it can be determined from the external photoluminescence quantum yield (EQE$_{PL}$). We evaluate the $V_{OC}$ defect by comparing the calculated QFLS to their theoretical maximum $V_{OC}$ (in the absence of non-radiative recombination). The use of quantitative PL for calculating the $V_{OC}$ defect enables the possibility to use it in bare absorbers, powders or single crystals. This allows for differentiation of non-radiative recombination losses introduced by other layers of a solar cells stack or by the presence of grain boundaries.

We use hyperspectral quantitative PL imaging to characterize several kesterite type materials in the form of thin films, powders and single crystals. One of the recent strategies tested to overcome the $V_{OC}$ deficit limitation of kesterites has been the partial replacement of Cu, Zn and Sn cations by other elements. We also analyzed the effect in the QFLS of the incorporation of several elements in kesterite-photo voltaic materials, including Li and Ge in high efficiency solar cells and Ag in CZTSe powders. We observe that the EQE$_{PL}$ increases by the incorporation of Ag and Li in CZTSSe. Based on our results we propose some recommendations to further reduce non-radiative recombination and the $V_{OC}$ deficit in kesterite solar cells by cationic substitution.

11:45 AM ES20.09.05
Composition-Dependent Charge Carrier Dynamics at Mg$_{x}$Zn$_{1-x}$O/CdTe Interface

Niraj Shrestha, Geethika K. Liyanage, Adam Phillips, Michael Heben and Randy J. Ellingson; The University of Toledo, Toledo, Ohio, United States.

Recent studies have shown that correct conduction band alignment at the emitter/absorber interface in photovoltaic devices leads to reduced interface recombination and higher device performance. Mg$_{x}$Zn$_{1-x}$O (MZO) is an interesting choice for the emitter because (1) it is a wide bandgap material that will not absorb photons and (2) the conduction band can be controlled by changing the Mg concentration. Consequently, MZO is being incorporated into CdTe devices. Unfortunately, few groups have demonstrated the improved device performance when using MZO alone. This suggests that the band alignment is not correct or new interface defects are being introduced. Here we investigate the carrier lifetime of sputtered CdTe devices using steady-state and time resolved photoluminescence spectroscopy (TRPL). Our preliminary results show that carrier lifetime increases as the bandgap of the MZO increases from 3.4 eV to 3.7 eV. We attribute the reduction of interfacial recombination to improved band bending in the CdTe as a function of better band alignment between MZO and CdTe. We will extend our study to determine if the conduction band alignment alone is responsible for reduced recombination by varying the MZO dopant density. We will show that TRPL can be a quick tool to determine if appropriate band alignment and bending have been achieved.

SESSION ES20.10: Calculation and Prediction
Session Chairs: Veronique Gevaerts and Dragica Vasileksa
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 132 B

2:00 PM *ES20.10.01
Disorder Effects in Photovoltaic Chalcogenides and Nitrdes
Stephan Lany; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

In multinary compound semiconductors, cation disorder can decisively alter the electronic properties and impact potential applications. Computationally, this problem can be addressed by a tiered approach, where we map total energies from density functional theory onto a model Hamiltonian, which can be subsequently used in Monte-Carlo simulations. The resulting disordered atomic structures are then fed back into first principle calculations for the electronic structure, yielding properties such as the band gaps and optical spectra, and the inverse participation ratio describing localization in the density of states. This presentation will review recent work on disorder effects in chalcogenides, such as Cu$_2$SnS$_3$ and Cu$_2$ZnSnS$_4$,[1] and the photovoltaic ZnSnN$_2$[2]. We will further touch upon new nitrdes of potential interest to photovoltaics, such Mg3SBN and candidates emerging from a broader nitrde search.[3]


2:30 PM ES20.10.02
Predicting Defect Formation Energies from Statistical Learning of Bulk Properties
Amit Samanta, Joel B. Varley and Vincenzo Lordi; Lawrence Livermore National Laboratory, Livermore, California, United States.

Point defects play an important role in determining a wide variety of materials properties and detailed analyses of their role often necessitates the evaluation of their formation energies and transition levels. Generally, formation of point defects involves displacing few atoms from their ideal positions meaning that defect formation is very localized process that involves very little degrees of freedom of a system. In this talk, I will illustrate how machine learning techniques can be used to predict formation energies and transition levels of native defects in III-V and II-VI semiconductors with a quantifiable uncertainty using a set of simple descriptors, like branch point energy and dangling bond energies. These descriptors can capture local neighborhood information as well as structural information and can be evaluated easily from ab initio simulations. Our analysis opens avenues for predicting the stability of defects in complex materials and alloys by training a coarse-grained model which can significantly simplify experimental design and material synthesis.

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

2:45 PM ES20.10.03
Machine Learned Defect Level Predictor for Cd-Based Chalcogenides
Arun Kumar Mamodi Kanakkithodi, Michael Davis and Maria K. Chan; Argonne National Laboratory, Argonne, Illinois, United States.

Impurities and defects in the band gap are critically important in photovoltaic (PV) materials, including thin film chalcogenides, as recombination centers, dopants, or passivants. Predicting formation energies and charge transition levels for defects in these PV materials is thus paramount; density functional theory (DFT) calculations have been widely applied for such studies. However, the requirement of large supercells and inclusion of charged states make these computations very expensive, and trends and knowledge from previous calculations are not exploited in subsequent ones. In this work, we use DFT to generate a substantial computational dataset of the formation energies and transition levels of vacancy, interstitial and substitutional point defects in Cd-based pure and alloyed chalcogenide systems (CdX, where X is O or a combination of S, Se, Te). The hybrid HSE06 functional is used for these calculations to correct for the band gap and band edge miscalculation that is characteristic of the standard PBE functional for this class of materials. We then apply machine learning techniques to extract crucial design rules and predictive models from the data, via the intermediate process of numerically representing any defect in terms of easily calculated structural and electronic properties of defect atoms, their known compounds, and using information from cheaper, lower-fidelity calculations. Using correlation analysis and regression techniques, we obtain accurate predictive models for formation energy and every relevant transition level that require only a handful of descriptors as input. These models are used to make predictions for defect energy levels in thousands of unexplored cases, such as Cd(Se,Te) which is of current interest, thus expanding our knowledge to wide areas of the chalcogenide chemical space. The machine learning strategy used here can lead to a framework for accelerated prediction of defect properties and allow efficient materials design for performance improvements in Cd-chalcogenides as well as other PV materials.

3:00 PM BREAK

SESSION ES20.11: Module Fabrication and Stability
Session Chairs: Amit Munshi and Mario Ochoa
Cadmium telluride (CdTe) solar cells have been researched for decades and through this time very few key technological step changes have been critical to its success: I. the superstrate process that forms a buried passivated junction, II. the annealing in a chlorine containing atmosphere, III. a stable copper back-contact, and IV. the introduction of selenium to grade the absorber structure. First Solar’s thin-film CdTe solar cells have been certified at 22% cell efficiency. The presentation will review our understanding of the performance limiting mechanisms and opportunities to further improve efficiency. Desirable improvements often conflict with established processes and material choices and this places significant constraints on the development of new technology components. One of these improvements, is to replace the p-type dopant in the absorber layer with a dopant from the 5th column of the periodic table. Over the last two years, First Solar has made steady progress on realizing a Group-V doping in polycrystalline CdTe and the first milestone was the consistent demonstration of greater than 10% cm² hole concentration with a flat doping profile and narrow depletion width. It has been challenging to produce the desired improved Voc with an alternative dopant and we will review evidence that may point to a direction on how to overcome the limitations.

First Solar’s leading thin-film manufacturing capabilities are in process of ramping the new utility-power optimized Series 6 module. Series 6 modules will have power ratings up to 440 Watts with an optimized design to lower installation and other balance of system cost. It will preserve First Solar existing CdTe module power density advantage superior temperature coefficient, spectra and shading response.

As CIGS PV technology has matured to production on an industrial scale, its long-term stability becomes increasingly important. The electric yield and thus the revenue of a PV system depend on both the initial conversion efficiency as well as its development over time. Increasing this long-term stability by understanding and lowering the degradation of CIGS technology is therefore a key strategy for its market success. Furthermore, increasing the long-term stability of individual solar cells allows to lowering the demands and thus the cost of barrier materials necessary for flexible CIGS modules. Literature has revealed that large differences in the stability of CIGS modules in the field have been observed. Therefore it is important to identify, predict and prevent degradation mechanisms.

An overview of degradation mechanisms occurring in CIGS solar cells and modules (observed in the laboratory and field experiments as obtained from literature) will be presented.

A first reason for the long term performance loss of CIGS solar cells and module is water ingress. Tests have shown that humidity can cause the increase of sheet resistance of the ZnO:Al front contact, while it can also deteriorate the interconnection conductivity, especially in the P2. Both effects can lead to an increased series resistance. Methods to mitigate the degradation of the ZnO:Al front contact on cell level are thicker layers, higher deposition temperatures, post deposition annealing, higher carrier concentrations and smoother underlayer substrates. The use of alternative TCOs like ITO and IO:H can also improve reliability. Moreover, the presence of humidity combined with a bias voltage can lead sodium migration, which can cause severe shunting. Strong effect of the sodium content on this degradation mechanism has been observed. Fortunately, most sources reveal that exposure to only elevated temperatures and illumination do not harm, or even improve solar cell performance.

Another degradation mechanism occurring in the field is power loss due to partial shading of CIGS modules. If one or several cells in a module are covered by e.g. bird dropping, humans, animals or trees, a reversal of the power flow can occur in the shaded area. In a module cells are connected in series, due to this series connection a current is forced through the shaded cells, resulting in a reversed power flow over the shaded cells, often referred to as negative or reversed bias. It was observed that very short shading events of seconds could lead to degradation of the modules.

Modules degraded due to partial shade show very typical symptoms, which are: Reduction of FF due to reduced Ideg/Isc ratio; Small dark spots in electroluminescence due to localized shunts corresponding with worm-like defects, visible by naked eye; Non-permanent effects were also observed: the electrical performance can either reduce and increase over time after exposure to reverse bias. This effect seems strongly dependent on the module type.

The reverse characteristics can be modified by a change in buffer layer composition and thickness, although the relation with degradation has up till now not been made.

Another degradation mechanisms that mostly has been observed in the field is Potential-Induced Degradation (PID). This is caused by the exposure of modules in the (negative) end of a string to voltages as high as 1000 V. PID has been identified on CIGS modules by a combination of electroluminescence and IV measurements. PID is also a common defect for crystalline silicon modules, where it is associated with sodium migration, mostly from the front glass. For CIGS, the sodium could originate from the substrate glass.

In the present study, standard cells of 0.5cm² of the mini-module are compared to that of small-area cells, additional characterizations (SEM, Raman, XPS, XRD) were performed and led to the following hypotheses. As all of the layers composing the devices (i.e. small cell and mini-module) were grown simultaneously, the parameters potentially explaining the observed lowered Voc/cell (mini-module) relative to that of small-area cells, additional characterizations (SEM, Raman, XPS, XRD) were performed and led to the following hypotheses. As all of the layers composing the devices (i.e. small cell and mini-module) were grown simultaneously, the parameters potentially explaining the observed lowered Voc/cell of the mini-module are reduced to that of small-area cells, additional characterizations (SEM, Raman, XPS, XRD) were performed and led to the following hypotheses. As all of the layers composing the devices (i.e. small cell and mini-module) were grown simultaneously, the parameters potentially explaining the observed lowered Voc/cell of the mini-module are reduced to that of small-area cells, additional characterizations (SEM, Raman, XPS, XRD) were performed and led to the following hypotheses. As all of the layers composing the devices (i.e. small cell and mini-module) were grown simultaneously, the parameters potentially explaining the observed lowered Voc/cell of the mini-module are.

The photovoltaic performance demonstrated here in this alternative architecture opens new routes to drastically decrease the gap observed between small-area-cells and industrial modules.

Cu(In,Ga)(S,Se)² based thin-film solar cells have recently achieved the outstanding performance of 22.9% efficiency at the laboratory scale. In contrast, the best performance of CIGS solar commercial modules does not exceed 15.5%. Such a difference is partially inherent to the actual architecture of the modules (P1, P2, P3 patterning), leading to a decreased active area, an increased series resistance as well as optical losses due to the decreased sheet resistance of the transparent conductive oxide (e.g. ZnO:Al). To overcome these limitations, we propose a modified architecture of modules where the cells are interconnected via metallic grids. This monolithic approach consists in using Ni/AlNi grids to electrically connect the rear contact of the cell N to the top window layer of the cell N+1. Independently of absorber band gap energy, this architecture allows (i) increasing the width of the cells, thereby decreasing the surface ratio of inactive area and (ii) decreasing the thickness of the ZnO:Al layer without resistive losses, thereby minimizing the optical losses.

In the present study, standard cells of 0.5cm² and alternative modules composed of 3 cells connected in series are investigated. The most impressive result concerns the FF achieved with the alternative module, which reaches the value of 81%, yielding an active area efficiency of 17.2%. The Voc of the alternative module is 2.05 V (i.e. 684 mV per cell), which is close but still lower than the Voc of the standard small-area cell (702 mV). In order to further explore the potential origins of such lowered Voc/cell (mini-module) relative to that of small-area cells, additional characterizations (SEM, Raman, XPS, XRD) were performed and led to the following hypotheses. As all of the layers composing the devices (i.e. small cell and mini-module) were grown simultaneously, the parameters potentially explaining the observed lowered Voc/cell of the mini-module are.

The photovoltaic performance demonstrated here in this alternative architecture opens new routes to drastically decrease the gap observed between small-area-cells and industrial modules.
zone. The size of the dead zone is typically in the range of ~350 um for commercial modules. The ratio between this dead zone and the small cell size is one of the factors that play a large role in the cell to module losses. The selective removal steps or scribes that are present in the monolithic interconnection can be made using laser scribing (P1, P2) or mechanical patterning (P2, P3). Laser scribing has the advantage of precision and lesser peripheral damage as compared to mechanical scribe. Industrially also laser scribing is preferred due to wear of the needle in mechanical patterning. Higher yield and smaller dead area in the interconnection make that successful laser scribing is important for improvement of the module efficiency.

In the monolithic interconnection the P1 scribe separates the metal back contact and is typically done with a laser. The P2 creates the connection between the bottom and top contact of neighboring cells and both laser as well as mechanical scribes are used. The P3 that isolates the top contact (TCO) of the cells is typically made using a mechanical scribe. Laser scribing of the P3 however is challenging because CIGS is very thermally sensitive. It has been shown that laser patterning of CIGS induces formation of conductive species. These conductive species create shunts in the scribe that are detrimental to the efficiency [1].

In this work we show the use of Raman spectroscopy for identification of shunt-free P3 scribe using a pulsed laser. Ablation of the TCO is the minimum requirement to form the P3, but removal of CIGS is an added advantage since CIGS has lateral conductivity. Melting of CIGS which leads to formation of conductive species needs to be avoided for good isolation in the P3.

Material removal by a typical laser scribing process involves rapid heating, melting and evaporation material. The thermal sensitivity of the CIGS can results in molten scribe edges, redeposition of conductive material and compositional changes within the layer next to the scribe. Different laser parameters were systematically studied for pulsed infrared laser scribing of CIGS including pulse duration, pulse overlap and laser fluency. Raman spectroscopy in conjunction with SEM, EDX and lock-in thermography was used to identify compositional changes in the area of the scribes.

In our research we have shown that Raman spectroscopy is a very suitable technique to monitor melting and shunt-free scribing in CIGS. We will explain our approach of using Raman line-scans over the laser scribe and the use of a contour plot. This approach allows for clear differentiation between shunted versus shunt-free scribes looking at the broadening of the main 177 cm⁻¹ CIGS peak and the appearance of a CIS peak at 290 cm⁻¹. Finally we show that shunt-free laser scribing of a P3 in CIGS is possible using a pulsed infrared laser.


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**SESSION ES20.12: Defects Characterization**

**Session Chairs:** Daniel Abou-Ras, Akira Nagaoka, Philipp Schöppe and Adele Tamboli

**Friday Morning, April 26, 2019**

**PCC North, 100 Level, Room 132 B**

**8:30 AM · ES20.12.01**

**Using Correlative EBIC-EBSD-APT to Identify Limitations in Cu(In,Ga)Se₂ Photovoltaic Cells**

*Jens Keutgen, Oana Cojocaru-Mirédin and Mohit Raghuwanshi; RWTH Aachen University, Aachen, Germany.*

Solar cells based on Cu(In,Ga)Se₂ (CIGS) present efficiency of up to 22.9% and is highest among other thin film photovoltaics, but considering Shockley-Queisser limit (33.7%) there is still a big room for improvement. Impressively, over the years, its maximum efficiency is achieved in its polycrystalline form, even with its small grain sizes of 2 μm. Previous studies have shown an important role of all grain boundaries (GBs) 2–4 towards its output efficiency. Here using electron beam induced current (EBIC) technique we found that most of the GBs are indeed beneficial for the device, however a small percentage (15%) of GBs was found detrimental. Hence, in this work we have isolated these detrimental GBs and perform correlative EBIC-EBSD and atom probe tomography (APT) on them to identify its type, structure and composition as shown in Figure 1. These results show that detrimental GBs are mainly enriched in Cu and O and depleted in Ga. Whereas characteristics of a beneficial GB are Cu depletion, no O and no change in Ga. With sufficient statistics, we have obtained characteristics of ‘detrimental’ GBs, which could be avoided in future by variation in deposition parameters and post deposition treatments.

References:


**9:00 AM · ES20.12.02**

**Suitable Complex S-Se Graded Bandgap Profiles on Kesterite-Based Solar Cells**

*Jacob Andrade-Arvizú, Victor Izquierdo-Roca, Ignacio Becerril, Pedro Vidal-Fuentes, Maxim Guc, Yudania Sánchez, Sergio Giraldo, Zacharie Jehl, Marcel Placidí, Alejandro Pérez-Rodríguez and Edgardo Saucedo; Solar Energy Materials and Systems, Catalonia Institute for Energy Research (IREC), Sant Adrià de Besós, Spain; IN2UB, Departament d’Electrònica, Universitat de Barcelona, Barcelona, Spain.*

Graded band concepts have been shown to be a disruptive issue in order to achieve high efficiency devices in thin film chalcopyride photovoltaics. In the case of kesterite (Cu₂ZnSn(S,Se)₄ or CZTSe) in short) based solar cells, two main strategies are being explored in order to achieve bandgap grading: cationic substitution (Cu by Ag, Zn by Cd, Sn by Ge and Si) and anionic (S-Se) compositional engineering. Both the cationic and anionic substitutions are complementary as they primarily affect either the conduction (cation) or valence (anion) bands. The specific control of the anionic composition along the volume of kesterite absorbers has been found challenging due to the similar formation energy of selenide and sulfide compounds that favors S-Se solid solutions over phase segregation. This work presents the development of a novel and non-toxic reactive annealing process that allows the synthesis of CZTSe solar cells with S-Se sharp graded compositional profiles and sheds light onto the dynamics of anionic bandgap grading in kesterite solar cells. By using different sources (pure S > CH₃S > SeS > SnS, ordered by expected reactivity), testing to control perfectly the S and Se content of the final CZTSe layers and to form an S-enriched top surface. After an optimization of the annealing parameters, we demonstrate the feasibility of a graded composition CZTSe phase with high S content at the top by introducing pure S during the cooling down process of the CZTSe kesterite. Multi-wavelength depth-resolved Raman spectroscopy measurements allowed to characterize the complex graded structure and estimate the composition of the CZTSe layers. A bandgap > 1.20 eV within the depletion zone and ≤ 1.03 eV towards the back contact interface is obtained this way. These results are correlated with in-depth Auger Electron Spectroscopy (AES), Grazing Incidence X-Ray Diffraction (GIXRD) and X-ray fluorescence (XRF), confirming the possibility of achieving a complex graded anionic compositional, and therefore, graded bandgap profiles. The fabricated solar cell devices show conversion efficiencies > 9%, with a Voc deficit of 420 mV, which currently represent a promising result for non-optimized graded absorber. In summary, preliminary results in which the samples are first selenized and then, in-situ superficially sulfurized, show the possibility of creating an inverted grading profile with higher bandgap towards the surface of the absorber by using pure elemental S source. We will show that obtaining S-Se graded bandgap profiles (both at the front and back interfaces) is only possible when the S is introduced in an out-of-equilibrium state. Strategies for achieving more complex graded bandgap profiles will be discussed including effects on device performance using experimental analysis by SCAPS modeling.

**9:15 AM · ES20.12.03**

**Control of the Composition of CZTSe Absorber Material and Its Influence on Solar Cell Performance**

*Teoman Taskesen, David Nowak, Vincent Steininger, Devendra Pareek, Wenjuan Chen, Jörg OHland, Ulf Mikolajczak and Levent Gümey; University of Oldenburg, Oldenburg, Germany.*

Up to date, kesterite has drawn a significant attention as an absorber material for future photovoltaic applications. Recent research aims at understanding the nature of this quaternary material and intends to improve the device efficiency further. In this work, we performed a compositional study on CZTSe kesterites grown by a two-step process. Films are processed by sputtering of precursors containing elemental Zn and alloyed CuSn layers, and an annealing procedure at 530 °C under selenium atmosphere, additionally...
placing elemental Sn within the susceptor. We distinguish two mechanisms for composition control and demonstrate their tuning for optimization of the absorber fabrication process. A direct composition control can be achieved in the classical manner by varying the sputtering duration for each layer of the stack. Another indirect control parameter is the tuning of the selenium amount: This is found to impact the final composition of the absorber by i) stabilizing the formation reaction of CZTSe, ii) hindering possible SnSe loss from the CZTSe absorber at high temperatures, and iii) reacting with the elemental Sn in the selenization chamber to SnSe, assisting for the incorporation of additional Sn into the film via SnSe, vapour. Each of these three mechanisms appears to be influenced by the amount of Se available in the chamber. Elemental analysis of the grown absorbers shows a variation of the Cu/Zn and Zn/Sn ratios in the range of 0.9:1.6 and 1.2:1.2 respectively. Solar cell results demonstrate that the studied system is highly tolerable for the compositional variations, showing device efficiencies between 9 and 11% even at significantly off-stoichiometric compositions. By fine-tuning the discussed parameters, improved solar cells were obtained reaching a $V_{OC}$ of 476 mV for pure selenium kesterite and device efficiencies around 12%.

9:30 AM *ESE20.12.04
II-IV-V$_2$ Semiconductors—Cation Order-Disorder Properties and Photovoltaic Applications Adele Tamboli$^{1,2}$, Angela Fioretti$^1$, Celeste Melamed$^2$, Rekha Schnepf$^2$, Aaron Martinez$^2$, Jie Pan$^1$, Ann Greenaway$^1$, Allison Mis$^2$, Elisabeta Are$^1$, Andryz Zukatayev$^1$, Laura T. Schellhas$^2$, Eric Toberer$^2$ and Stephan Lany$^2$; 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Colorado School of Mines, Golden, Colorado, United States; 3SLAC National Accelerator Laboratory, Menlo Park, California, United States.

II-IV-V$_2$ semiconductors such as ZnSnN$_2$ and ZnSiP$_2$ offer the promise of optoelectronic properties on par with the III-Vs combined with the tunability of complex multinary materials like CIGS, due to their ternary composition and ability to control cation order parameter. For example, ZnSnN$_2$ has been predicted to exhibit band gap tunability from 1.1-1.5 eV based on variation in cation disorder, which arises mainly from local violations of the octet rule, with band gap narrowing occurring when N-centered motifs deviate from their ideal 2Zn + 2Sn coordination. Other II-IV-V$_2$ materials such as ZnSiP$_2$, ZnGeP$_2$, and ZnGeN$_2$ exhibit similar phenomena. The nitride materials of this family exhibit defect tolerant behavior and are photoactive as polycrystalline thin films, while the phosphides are lattice-matched to Si, and can be grown epitaxially for tandem photovoltaic applications. We have grown thin films of several nitride and phosphide members of this family and have observed strong photoluminescence behavior, promising energy conversion properties in a photoelectrochemical configuration, and tunable carrier concentration. This talk will focus on experimental methods for synthesis and characterization of these materials (including combinatorial methods), evidence of their potential for photovoltaic applications, and calculations that provide a physical understanding of disorder and its impact on relevant properties.

10:00 AM BREAK

10:30 AM *ESE20.12.05
Quantitative Evaluation of Metastability Mechanisms in CIGS Solar Cells Marco Nardone$^3$, Yasas Patikirige$^1$, Curtis Walkons$^4$, Shubhra Bansal$^2$, Theresa Friedlmeier$^3$, Oliver Salomon$^3$, Kyoung E. Kweon$^3$, Joel B. Varley$^1$ and Vincenzo Lordi$^3$; 1Bowling Green State University, Bowling Green, Ohio, United States; 2University of Nevada, Las Vegas, Las Vegas, Nevada, United States; 3Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Stuttgart, Germany; 4Materials Science, Lawrence Livermore National Laboratory, Livermore, California, United States.

Copper Indium Gallium Diselenide (CIGS) photovoltaic devices usually exhibit variations in device performance when exposed to heat, voltage bias, and/or light. The degree of such variations and their reversibility depends on fabrication processes and impurity concentrations. Typically, light soaking at elevated temperatures increases the apparent doping concentration and open circuit voltage while heating in the dark tends to reverse those gains. Although the underlying mechanism is not clear, this metastable behavior is often attributed to transitions of the copper-selenium (V$_{Cu}$-V$_{Se}$) divacancy defect between donor and acceptor states. A better understanding of metastability could improve the utility of test standards and suggest pathways to increase power conversion efficiency.

In this work, physical models of metastability are quantitatively evaluated by comparison to current density-voltage (JV) data collected in situ during light soak at various temperatures and applied bias. Our time-dependent JV data at different stress conditions provide a unique platform for testing mechanistic hypotheses. Additional insight is gained by comparing CIGS devices with either CdS or Zn(O,S) buffer layers. Metastability mechanisms based on defect kinetics associated with lattice relaxations are coupled with semiconductor device simulations to predict how JV, quantum efficiency (QE), and capacitance voltage (CV) characteristics vary with time under specific stress conditions. The evaluated defect kinetics models include the ($V_{Cu}$-$V_{Se}$) divacancy complex with the previously calculated activation energies as well as more generic models of charge-induced shallow or deep defects. $Ab-initio$ calculations are also conducted to elucidate possible chemical species and lattice relaxation parameters.

Our results suggest that the ($V_{Cu}$-$V_{Se}$) divacancy model alone does not explain much of the observed metastability data due to the low transition energy barrier from the donor to acceptor state. Calculations with the generic defect models suggest that the data can be described by the formation of shallow acceptors upon electron capture with an activation energy close to 1 eV. In some cases, the formation of deep recombination centers with similar activation energy must also be evoked to account for losses in open circuit voltage during light soak at higher temperatures. In general, these types of mechanisms are associated with phenomena such as persistent photococonductivity and self-compensation when a system is sufficiently flexible to readjust in response to a shift away from equilibrium. In the case of metastability, it appears that electron injection in CIGS causes the system to respond by creating defects that reduce the electron concentration. This work quantifies the rates and magnitudes of the response.

Part of this work was conducted under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

11:00 AM *ESE20.12.06
Group-V Doping Limit in Cd-Rich CdTe for High Open-Circuit Voltage Akira Nagaoka$^{1,2,4}$, Darius Kuciauskas$^3$, Kenji Yoshino$^3$, Yoshitaka Nose$^3$, Kensuke Nishikawa$^3$ and Mike Scarpulla$^3$; 1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan; 2Department of Applied Physics and Electronic Engineering, University of Miyazaki, Miyazaki, Japan; 3National Renewable Energy Laboratory (NREL), Golden, Colorado, United States; 4Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah, United States.

Both group-V element doping and Cd-rich composition are important techniques for overcoming the open-circuit voltage deficiency in CdTe photovoltaic device by improvements of both p-type doping and long minority carrier lifetime. However, group-V doping simultaneously involves the formation of AX compensating donor like defect which results in low doping activation.

We present a comprehensive experimental approach to reveal equilibrium As doping limit of a few times $10^{17}$ cm$^{-3}$ in Cd-rich CdTe by very gentle cooling process. As-doped Cd-crich CdTe single crystal with high hole concentration $> 10^{17}$ cm$^{-3}$ and long bulk lifetime $> 20$ ns can be obtained. We demonstrate CdTe photovoltaic device with high open-circuit voltage of 900 mV by As-doped Cd-rich bulk single crystal as absorbing layer. These results indicate that group-V doping and Cd-rich composition enable the improvement of optical and microstructure deficiency in CdTe photovoltaic device.

11:30 AM ES20.12.07
Effects of Alkali Metal Impurities on Metastability Mechanisms in CuInGaSe$_2$ Solar Cells Kyoung E. Kweon$^3$, Amit Samanta$^1$, Joel B. Varley$^1$, Vincenzo Lordi$^3$, Curtis Walkons$^4$, Shubhra Bansal$^2$, Marco Nardone$^3$, Yasas Patikirige$^1$, Theresa Friedlmeier$^3$ and Wolfim Hempel$^3$; 1Lawrence Livermore National Laboratory, Livermore, California, United States; 2Mechanical Engineering, University of Nevada, Las Vegas, Las Vegas, Nevada, United States; 3Physics and Astronomy, Bowling Green State University, Bowling Green, Ohio, United States; 4Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Stuttgart, Germany.

Cu(In,Ga)$_{2}$Se$_{3}$ (CIGS)-based solar cell has yielded the highest light-to-electrical energy conversion efficiency of all thin-film solar cells. To achieve a high conversion efficiency, incorporation of alkali metal (AM) impurities in CIGS has become critical. In addition, light induced and voltage-bias induced metastabilities could further enhance the performance of p-type CIGS by increasing hole concentration. However, the relationship between AM impurities and positive light/voltage-bias induced metastabilities is not well understood and remains largely explored. However, it has been experimentally observed that a large amount of AM impurities segregate at grain boundaries and the absorber/buffer interface, but they can diffuse into the grain depending on the growth conditions or over long aging times. Therefore, analysis of AM impurities both in the grain and at the grain boundaries are important to elucidate their role on metastabilities.

In this work, we performed first principles calculations with a hybrid functional to explore effects of AM impurities on electronic properties of CuInSe$_2$ (CIS), particularly on light-induced metastabilities. First, we calculated binding interaction between AM and divacancy complexes ($V_{Cu}$-$V_{Se}$), which has been speculated to exhibit metastable properties in
CIGS. We found that formation of \( (\text{V}_{\text{Cu}}-\text{AM}_{\text{Cu}}) \) complexes, in which AM is located at the \( \text{V}_{\text{Cu}} \) site, is energetically favorable. The binding energy of the \( (\text{V}_{\text{Cu}}-\text{AM}_{\text{Cu}}) \) complexes with respect to the \( (\text{V}_{\text{Cu}}-\text{F}_{\text{Cu}}) \) and \( \text{AM}_{\text{Cu}} \) increases in order of increasing atomic size of AM (Na < K < Rb). Similar to the \( (\text{V}_{\text{Cu}}-\text{F}_{\text{Cu}}) \) complex, the \( (\text{V}_{\text{Cu}}-\text{AM}_{\text{Cu}}) \) complexes also have different donor and acceptor configurations, and conversion between these two stable configurations can occur by overcoming energy barriers accompanied by accepting electrons/relieving holes. Our calculations predict that the required energy for the forward reaction (donor to acceptor conversion) is 0.16, 0.42, and 0.60 eV eV for the \( (\text{V}_{\text{Cu}}-\text{Na}_{\text{Cu}}) \), \( (\text{V}_{\text{Cu}}-\text{K}_{\text{Cu}}) \), and \( (\text{V}_{\text{Cu}}-\text{Rb}_{\text{Cu}}) \), respectively, which is larger than 0.05 eV for the \( (\text{V}_{\text{Cu}}-\text{F}_{\text{Cu}}) \). This suggests that formation of the metastable acceptor configuration would be largely suppressed for the \( (\text{V}_{\text{Cu}}-\text{AM}_{\text{Cu}}) \) complexes with heavier AM.

Second, we examined geometries, energetics, and electronic structures of \( \text{AM}_{\text{Cu}} \) and its associated defect complexes at grain boundaries. Among many possible grain boundaries, we constructed \( \{112\} \) twin boundaries (TB), which are commonly observed in CIGS. Three different \( \{112\} \) twin boundaries were found with different Se local coordination environment at the boundary; for the most stable TB, all Se atoms at the TB are regularly coordinated with 2 Cu and 2 In, while for the least stable TB, Se atoms at the TB are coordinated with either 3 Cu and 1 In or 1 Cu and 3 In. Our calculations demonstrate that the formation energy of \( \text{AM}_{\text{Cu}} \) decreases at all three TB considered in this work with respect to that in the bulk, while the amount of decrease is larger for the TB containing more irregularly coordinated Se atoms at the boundary. Also, we found that heavier AM has stronger tendency (Na < K < Rb) to segregate at the grain boundaries, which agree well with the experimental observations demonstrating that K or Rb locates at the grain boundaries by kicking out Na at the grain boundaries. Furthermore, \( \text{AM}_{\text{Cu}} \) interaction with other point defects and defect complexes will be discussed to understand more comprehensive effects of AM impurities at the grain boundaries.

11:45 AM ES20.12.08
Microscopic Effects of Light-Soaking for Cu(In,Ga)Se2 Solar Cells
Alexandra Nikolaeva1, Maximilian Krause1, Wolfram Witte2, Dimitrios Hariskos2 and Daniel Abou-Ras2; Helmholtz-Zentrum Berlin, Berlin, Germany; *Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Stuttgart, Germany.

Light-induced enhancement of the performance as a result of an increase of the open-circuit voltage and fill factor is widely observed in Cu(In,Ga)Se2 (CIGS) solar cells with Zn-compound buffer layers [1,2]. However, the reason for the improved efficiency is still under discussion. The present study was conducted in order to investigate the microscopic effects of light-soaking (LS) in Cu(In,Ga)Se2 solar cells with solution-grown CdS and Zn(O,S) buffer layers. Electron-beam induced current (EBIC) measurements were carried out before and after the LS under AM 1.5G illumination, as well as after keeping samples in the dark. In addition, cathodoluminescence and energy-dispersive X-ray spectrometry analyses were performed in order to gain insight into possible effects on the local radiative recombination and the elemental distribution. By evaluating EBIC profiles extracted perpendicular to the p-n junction, values for the widths of the space-charge regions, which are (roughly) proportional to \( \text{N}_{\text{v,0}} \) [3], and for the diffusion lengths of minority charge carriers were determined [4]. It is revealed that for solar cells with both, CdS/CIGS and Zn(O,S)/CIGS heterojunctions, the diffusion length increases significantly already after 30 min LS treatment. The doping density slightly increases during the LS process. In addition, the influence of electron-beam irradiation and heat-light soaking was investigated.

High Performance Triboelectric Nanogenerators for Continuous Self-Powered Electronics

Prof. Baik will first introduce the fabrication of triboelectric nanogenerators with high-output as well as the preparation of the triboelectric active materials. This will be followed by a review of the physical and chemical understanding for the mechanism to generate the high-output in terms of energy conversion efficiency. Prof. Baik will also survey the potential applications for the self-powered systems such as IOT sensors, filters etc.

10:00 AM BREAK

Triboelectric Nanogenerators for Internet of Things

This part will introduce the development of IoT and requirements of energy harvesting. Then, we will review the progress of materials, performance of triboelectric nanogenerators and other energy harvesters. Lastly, the demonstrations of TENGs for IoT Applications will be investigated with latest research achievements. The trend of IoT, TENGs and energy harvester technology will be discussed.

11:15 AM

Implantable and Wearable Self-Powered Medical Electronics

This part will first demonstrate the first in vivo mechanical energy harvester and devices. We will then show a pacemaker prototype for controlling the frequency of heartbeat for the first time. Finally, Prof. Li will demonstrate other applications as real-time acquisition and wireless transmission of self-powered cardiac monitoring data. These works are concentrated on live-powered implantable medical devices.

1:30 PM

Piezotronic Effect for Efficient (Photo)Electrochemical and Catalyst Applications

This part will first discuss the fundamental principles of applying the piezotronic effect in engineering the interfacial band structure. Practical systems that implement the piezotronic enhancement will also be discussed. At last, Prof. Wang will show that piezoelectric potential can raise the energy of electrons at the surface of piezoelectric material (or electrode) to such a level that is sufficient to drive proton reduction reactions within its immediate vicinity.

2:15 PM

Piezotronics for 2D Materials

This part will first elaborate on the fundamental physics and material science of the piezotronic effect in 2D materials, which serve as the basis for understanding and utilizing the interfacial and charge carrier engineering in 2D piezotronics. Prof. Wu will then discuss the latest progress in the fundamental exploration and technological advances in 2D materials piezotronics. Finally, Prof. Wu will provide a perspective of this rapidly-advancing field.

3:00 PM BREAK

3:30 PM

Piezo-Phototronics of 3rd Generation Semiconductor

This part will first introduce the framework of the piezo-phototronic effects in III-Nitrides quantum well. Furthermore, Prof. Hu shall survey the carrier dynamic process in piezo-phototronic effects with the transit piezophototronic model and the time-resolved photoluminescence. Finally, Prof. Hu will discuss the applications of piezo-phototronic effect on III-Nitrides visible light communications, micro LEDs and solar cells.

4:15 PM

Principle and Luminescence Application of Piezo-Photonics

This part will first introduce physical mechanisms of piezo-photonics. Some host materials and metal-ion activators will be described for demonstrating piezo-photonic effect. Prof. Hao will then provide a unified profile and recent prototypical demonstrations of light-emission triggered by various mechanical stimuli. Finally, Prof. Hao will discuss the challenges and perspectives of this research field.

SYMPOSIUM ES21

Nanogenerators and Piezotronics

April 23 - April 26, 2019

Symposium Organizers

Jianhua Hao, The Hong Kong Polytechnic University
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* Invited Paper
Piezoelectricity, a phenomenon known for centuries, is an effect that about the production of electrical potential in a substance as the pressure on it changes. For wurtzite structures such as ZnO, GaN, InN and ZnS, due to the polarization of ions in a crystal that has non-central symmetry, a piezoelectric potential (piezopotential) is created in the crystal by applying a stress. The effect of piezopotential to the transport behavior of charge carriers is significant due to their multiple functionalities of piezoelectricity, semiconductor and photon excitation. By utilizing the advantages offered by these properties, a few new fields have been created. Electronics fabricated by using inner-crystal piezopotential as a "gate" voltage to tune/control the charge transport behavior is named piezotronics, with applications in strain/force/pressure triggered/controlled electronic devices, sensors and logic units. This effect was also extended to 2D materials such as MoS$_2$. Piezo-phototronic effect is a result of three-way coupling among piezoelectricity, photonic excitation and semiconductor transport, which allows tuning and controlling of electro-optical processes by strain induced piezopotential. The objective of this talk is to introduce the fundamentals of piezotronics and piezo-phototronics and to give an updated progress about their applications in energy science (LED, solar) and sensors (photodetector and human-CMOS interfacing).


Sustainable Power Generation from Multifunctional Triboelectric Nanogenerators Sang-Woo Kim; Sangkyunkwan University, Suwon, Korea (the Republic of).

Energy harvesting systems based on triboelectric nanomaterials are in great demand, as they can provide routes for the development of self-powered devices which are highly flexible, stretchable, mechanically durable, and can be used in a wide range of applications. Our recent research interest mainly focuses on the fabrication of high-performance triboelectric nanogenerators (TENGs) based on various kinds of nanomaterials. Flexible TENGs exhibit good performances and are easy to integrate which make it the perfect candidate for many applications, and therefore crucial to develop. In this presentation, I firstly introduce the fundamentals and possible device applications of TENGs, including their basic operation modes. Then the different improvement parameters will be discussed. As main topics, I will present a couple of recent achievements regarding highly stretchable transparent flexible TENGs, textile-based wearable TENGs, highly robust and efficient TENGs with multifunctional materials, etc. The recent research and design efforts for enhancing power generation performance of TENGs to realize self powering of portable and wearable sensors and electronics will also be discussed in this talk. Finally I am going to introduce a graphene triboelectronic touch sensor which is based on coplanar coupling of a single electrode mode TENG (S-TENG) and a graphene FET. When any object (e.g. human finger) comes into contact with friction layer of the S-TENG, the charges are produced due to well-known triboelectric effect. The triboelectric charges act as a gate bias to the graphene FET and modulates its current transport. The triboelectric sensors have displayed a sensitivity of ~2 % kPa$^{-1}$, a limit of detection <1 kPa, and a response time of ~30 ms. Furthermore, the devices can effectively detect touch stimuli from both bare and gloved fingers which can be a limitation with capacitive touch screens.

Theoretical Potential for Low Energy Consumption Phase Change Memory Utilizing Electrostatically-Induced Structural Phase Transitions in 2D Materials Evan Reed, Daniel A. Rehn, Yao Li and Eric Pop; Stanford University, Stanford, California, United States.

Structural phase-change materials are of great importance for applications in information storage devices. Thermally driven structural phase transitions are employed in phase-change memory to achieve lower programming voltages and potentially lower energy consumption than mainstream nonvolatile memory technologies. However, the waste heat generated by such thermal mechanisms is often not optimized and could present a limiting factor to widespread use. The potential for electrostatically driven structural phase transitions has recently been predicted and subsequently reported in some two-dimensional materials, providing an athermal mechanism to dynamically control properties of these materials in a nonvolatile fashion while achieving potentially lower energy consumption. In this work, we employ DFT-based calculations to make theoretical comparisons of the energy required to drive electrostatically-induced and thermally-induced phase transitions. Determining theoretical limits in monolayer MoTe$_2$ and thin films of Ge$_2$Sb$_2$Te$_5$, we find that the energy consumption per unit volume of the electrostatically driven phase transition in monolayer MoTe$_2$ at room temperature is 9% of the adiabatic lower limit of the thermally driven phase transition in Ge$_2$Sb$_2$Te$_5$. Furthermore, experimentally reported phase change energy consumption of Ge$_2$Sb$_2$Te$_5$ is 100–10,000 times larger than the adiabatic lower limit due to waste heat flow out of the material, leaving the possibility for energy consumption in monolayer MoTe$_2$ at room temperature of 9% of the adiabatic lower limit of the thermally driven phase transition in Ge$_2$Sb$_2$Te$_5$. Furthermore, experimentally reported phase change energy consumption of Ge$_2$Sb$_2$Te$_5$ is 100–10,000 times larger than the adiabatic lower limit due to waste heat flow out of the material, leaving the possibility for energy consumption in monolayer MoTe$_2$-based devices to be orders of magnitude smaller than Ge$_2$Sb$_2$Te$_5$-based devices.
Multifunctional ZnO and BaTiO3 Based Electro-Active Thin Films

Walker Tuff1, Yuyuant Xie2, Saquib Ahmed3 and Sankha Banerjee1; Mechanical Engineering, California State University, Fresno, Fresno, California, United States; Mechanical Engineering, Buffalo State College, Fresno, California, United States.

Electrical impedance spectroscopy (EIS) has been recognized as a powerful diagnostic tool for its extraordinary sensitivity. It has been widely used in evaluating electrical properties of materials and their interfaces with surface-modified techniques. Typically, EIS test applies a harmonic voltage perturbation to the target, then measures the response current, which can yield invaluable information of material electrical properties and structures as so-called impedance spectroscopy. In practical, impedance spectroscopy measurement on a multifunctional piezoelectric composite material is conducted through probing two electrodes at specific point or surface, while the specification of probing sites is generally arbitrary. The following work deals with the impedance tomography based characterization of ZnO/ZnO nanowire epoxy-BaTiO3 thin films with a variation in ZnO volume fraction from 1-10%. Impedance tomography data will also be used for generating dependent and independent data sets towards data analytics based optimization of surface properties and development of fabrication-process-property relationships. The surface micro-structure and topography will analyzed using scanning electron microscopy and profilometry. The piezoelectric and piezoelectric properties of these composites will also be characterized.

2:00 PM *ES21.02.03
Piezotronic/Piezophototronic Based Sensors and Applications

Junyi Zhai1, 2; Beijing Institute of Nanoenergy and Nanosystems, CAS, Beijing, China; Center on Nanoenergy Research, Guangxi University, Nanning, China.

Multifunctional micro/nano devices and systems are of important applications in smart electronics for health care, human-machine interfacing, infrastructure monitoring and security. In recent years, piezophototronic effect is developed fast since it offers a new method to improve/tune the optoelectronic properties dramatically. The key characteristic of the piezophototronic/phototronic effect is that the carrier generation, transport, separation and/or recombination at the heterojunction/interface can be tuned by modulating the piezopotential created and further tuned by externally applied strain. Piezophototronic effect can enhance the sensitivity of photodetector dramatically. Here, we show a self-powered GaN flexible film-based metal-semiconductor-metal (MSM) UV photoswitch. The asymmetric MSM structure was designed to suppress carrier recombination and enhance carrier transport. At self-powered condition (no external bias voltage), its UV on/off ratio reaches up to 4.67*104 with high reliability of on/off switching response. Also its UV detection shows an excellent sensitivity (1.78*107 cm²V-1W-1). In particular, strain modulation can improve the UV on/off ratio (~154%) by piezo-phototronic effect. Besides photosensitive conversion and electroluminescence, photoluminescence can be tuned by piezoelectric effect as well. Here we have developed a new method of pressure modulation by using pressure/stress induced piezoelectric effect to tune PL intensity of InGaN/GaN MQW under small strain (0–0.15 %). Such modulation effect is distinct, linear and ultrafast. Based upon it, an all optical pressure sensor array by the piezophototronic effect has been developed to measure dynamic pressure distribution without the need of electricity. Beyond the limitations of optical connection, our all-optical device offers a novel and suitable way for large-area, high-uniform, high resolution, ultrahigh speed pressure/strain distribution sensing. When combine piezotronic effect with magnetostriction, multi-field couplings can be realized. For example, magneto-optics and electro-optics, magneto-electrics and magneto-mechanics, piezotronics and piezophototronics, which could be of interest for fabricating functional devices in the fields of energy conversion, magnetic/optical imaging, high-density optical communication and information storage, smart sensing, and so on.

2:45 PM ES21.02.04
Piezo-Phototronic Effect in GaN Based Optoelectronic Devices

Weiguo Hu; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

As the third-generation semiconductors, III-Nitrides exhibits great potentials in the solid-state lighting, display, power device, photovoltaics and so on. The piezoelectric property is the great difference between III-Nitrides and previous semiconductors (Silicon, Germanium, etc.). Prof. Wang pointed out that the piezo-potential can be used as a gate to tune/control the carrier generation, transport, separation and/or recombination via external strain, and thus tuning the device performances [1].

This report focuses on piezophototronic effects in III-Nitrides. Firstly, in the framework of the quantum perturbation theory and constitutive equations, we proposed a self-consistent model to study the piezo-phototronic effects in quantum structures [2,3]. This model matches well with the optical excitation in InGaN/GaN quantum well under the various external stress field. Furthermore, we studied the carrier dynamic process in piezophototronic effects with the transit piezo-phototronic model and the time-resolved photoluminescence for the first time. The piezoelectric field was partly “canceled”, which increased the overlap of wavefunctions to decrease the carrier decay time. Thus, the maximum speed of a single chip was increased from 54 MHz up to 117 MHz in a blue LED chip under 0.14% compressive strain. Finally, the piezo-phototronic effect was used to effectively improve the conversion efficiency of InGaN/GaN quantum well and compensated the thermal degradation in high power InGaN/GaN micro-strip LED arrays [4,5].

These researches deepen our understanding on carrier’s excitation and transportation under external strain filed, and exhibits important applications in communication, lighting and energy collections.

Reference

3:00 PM BREAK
Piezotronics is a promising new class of semiconductor-devices that offer important implications for the realization of flexible nano-electronic, nano-sensor, and microelectromechanical (MEMS) applications. However, reproducibility in both synthesis and sensitivity has been a materials challenge for achieving wide-scale adaptation of these applications. We present a novel method for the synthesis and study of the piezoelectric effect of single-crystalline zinc oxide (ZnO) nanosheets (NS). Here we show reliable synthesis of free-standing two-dimensional (2D) nanometer thick ZnO achieved using Ionic Layer Epitaxy (ILE). In this method, a highly-packed surfactant monolayer guides crystal evolution underneath the ionized headgroups at the air-water interface. Using dynamic contact electrification force microscopy (DC–EFM) we measure the piezo response coefficient ($d_{33}$) of our as-synthesized NSs in the nanometer scale from 1 to 3 nm. The $d_{33}$ was found in the range of 10-60 pm/V. The thickness-related piezoelectric responses were studied as well. Comparing to reported piezo response values of bulk ZnO, the piezo response of our ZnO NSs offer significant implications for next-generation nanomaterials as building blocks for piezotronics.

### 4:15 PM ES21.03.03
**Stretchable and Wearable Triboelectric Nanogenerators for Human Machine Interface**

**Pooi See Lee**; School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore.

Harvesting energy from our environment or biomechanical motion requires the development of mechanical energy harvesting devices that are compliant to curvilinear surfaces or wearable on human body. Triboelectric nanogenerators (TENGs) generate electricity by triboelectrification and electrostatic induction from ambient energy that are ubiquitous and constantly available. Wearable TENGs based on textiles are attractive options as it can be incorporated onto garments and versatile for high portability. We developed two kinds of textile-TENGs, one for harvesting energy from water flow and another for harvesting biomechanical energy from human motion. An all-fabric-based dual-mode device harvests both the electrostatic energy and mechanical energy of water, achieving the maximum instantaneous output power density of 0.30 W m$^{-2}$. To generate energy from subtle biomechanical motion, an all-textile nanogenerator utilizing HCOEPNs encapsulated black phosphorus was presented with considerably high output (~250–880 V, ~0.48–1.1 mA cm$^{-2}$) with a small force (~5 N) and low frequency (~4 Hz), which can power small electronic gadgets. On the other hand, ionic based materials can be utilized to generate signal from touch and decode environmental changes. Based on the ionic conductive nanomaterials as building blocks for piezotronics.

### 4:45 PM ES21.03.04
**Self-Powered Motion Sensors and Monitoring Systems Based on Triboelectric Nanogenerator**

**Qingliang Liao**, Zheng Zhang, Zhuo Kang and Yue Zhang; University of Science and Technology Beijing, Beijing, China.

The advances in industry and information technology promote the development of internet of things and sensor technology. Self-powered systems based on energy harvesting technologies have been given significant attention with the increasing concern over energy crisis. Triboelectric nanogenorator (TENG) provides a novel mechanical energy harvesting technology and also can be used in the field of self-powered electronics. In this work, several kinds of self-powered electronics and system based on TENG were developed. Firstly, self-powered biomechanical motion sensors based on TENG were designed. Four kinds of TENGs with different structures were designed and the detecting properties of the fabricated biomechanical motion sensors were investigated. In order to meet the demands of actual application, the hybrid energy systems based on TENG were developed. A self-cleaning and self-charging power system based on an amphiphobic hydraulic TENG was constructed. A high-efficiency portable air filter enhanced by triboelectric effect was fabricated. These works represent a significant step for electronics and systems with superiorities of self-powered, high efficiency and low cost.

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**SESSION ES21.04: Piezoelectric and Triboelectric Nanogenerators III**

**Session Chairs: Jeong Min Baik and Pooi See Lee**

Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 132 C

**8:00 AM ES21.04.01**

**Large-Area Solution-Grown Two-Dimensional Tellurene for Smart, Ubiquitous Electronics**

**Yixiu Wang**, Gang Qiu, Ruxing Wang, Peide P. Ye and Wenzhuo Wu; Purdue University, West Lafayette, Indiana, United States.

The reliable production of two-dimensional (2D) crystals are essential for exploring new science and implementing novel technologies in the 2D limit. However, ongoing efforts are limited by the vague potential in scaling-up, restrictions in growth substrates and conditions, small sizes and/or instability of synthesized materials. Here we report the fabrication of large-area, high-quality 2D tellurene by a substrate-free solution process. The crystals exhibit process-tunable thicknesses from a monolayer to tens of nanometers, and lateral sizes up to 100 nm. The chiral structure of tellurene gives rise to strong in-plane anisotropic properties and giant thickness-dependent shifts in Raman vibrational modes, unseen in 2D layered materials. The tellurene transistors can exhibit air-stable performance at room temperature for over two months, with on/off ratios on the order of $10^2$ and field-effect mobility ~700 cm$^2$/Vs. More strikingly, with scaled channel length and integration with high-k dielectrics, the record-high on-state current density of 1.06 A/mm is demonstrated, surpassing all state-of-the-art 2D-based transistors. Our versatile solution process allows access to a broad range of characterization and application of tellurene as a new 2D semiconductor for high-performance, energy-efficient electronics in future ubiquitous applications.


**8:15 AM ES21.04.02**

**Conformal Piezoelectric Energy Harvesting and Storage from Motions of Internal Organs**

**Canan Dagdeviren**; Media Lab, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Implantable medical devices have made a major impact in improving healthcare. In recent years, these devices have increasingly become active rather than passive – for example, cardiac pacemakers are those of the active type. A key challenge for these active systems is their need for an internal electrical power source. A downside of present active systems is the limitation of their internal batteries, which are rigid, bulky and must be changed frequently, thus requiring recurring surgical procedures, with associated complication risks and additional healthcare costs. One compelling solution would be to employ energy harvesting as a means of recharging or completely replacing batteries for active implantable medical devices. Energy harvesting — through chemical reactions, heat extraction, blood flow, and natural mechanical movements of organs — could help address energy depletion issues in implantable devices. However, most energy harvesting units being considered today are like conventional batteries, in that they also rely on rigid electronics and subcomponents, and therefore, are incapable of providing intimate mechanical contact with soft tissue.
We have developed a new class of biocompatible piezoelectric mechanical energy harvesters (PZT MEHs) that are soft and flexible, with extremely low bending stiffness, allowing them to conform to and laminate on the heart as well as on other soft tissues. These devices are the first-of-its-kind flexible generators that convert mechanical energy from internal organ movements into electric energy to power medical devices. We designed and fabricated the entire device, and performed *in vitro* and *in vivo* tests, and analyzed the data to show that it is a feasible new invention. The co-integrated collection of such energy-harvesting elements with rectifiers and microbatteries provides an entire flexible system, capable of viable integration with the beating heart via medical sutures and operation with efficiencies of ~2%.

This conformal mechanical energy harvesters can yield significant amounts of electrical power from motions of internal organs, up to and exceeding levels relevant for practical use in implants. Under the rhythmic contraction of the heart muscle, the device bends and relaxes, enabling to supply enough trickle charge — a steady stream of charging current at low rate — to satisfy the needs of a pacemaker. Thus, this technology could extend the battery life of implanted medical devices or even eliminate the need of battery replacement that altogether would spare patients from repeated operations and the risk of surgical complications. Another potential application of this technology is in powering heart monitors/sensors worn epidemically on skin.

8:45 AM ES21.04.03
Fibre-Based Triboelectric Generators for Smart Textiles Using Surface-Modified Electrospun Polymer Fibres
Tommaso Busolo1, Daniel Ur1, Sung Kyun Kim2, Piotr Szewczyk1, Mateusz Marzec1, Andrzej Bernasik1, Urszula Stachewicz1 and Sohini Kar-Narayan2; 1Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, Krakow, Poland; 2Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; 3Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Krakow, Poland.

Wearable healthcare devices and point-of-care diagnostics are essential tools to provide affordable healthcare globally and to deliver personalised medicine. These devices are able to remotely monitor patient health in real time, thus improving diseases management and reducing medical cost. Furthermore, the physiological data collected can be used by a machine learning software to provide personalised treatments.

One of the biggest challenges that wearable technology faces is power supply[1]. In this context, triboelectric generators are promising as they rely on motion-generated surface charge transfer between materials with different electron affinities to convert mechanical energy, for example from body movements, into useful electricity. Fibre-based triboelectric generators are therefore particularly promising for wearable applications as they can harvest the kinetic energy from body motion and be seamlessly integrated into “smart” textiles at the same time. Current fibre-based triboelectric generators are limited by low power output. Two of the most effective methods to improve this are increasing surface area and altering the surface chemistry of the material. Higher surface area allows for higher charge transfer density, while tailored surface charge properties improve the charge transfer mechanisms. Electrospinning can be used to effectively tailor the surface chemistry of fibres by alternating voltage polarities in a single-step manufacturing process[2]. In our work, we have enhanced the triboelectric performance of poly(methyl methacrylate) and polyvinylidene fluoride by engineering both its surface area (due to the fibre geometry) as well as the surface chemistry (by controlling the polarity of applied voltage during electrospinning). Scanning electron microscopy and electrical measurements were used to study the effect of surface area enhancement. X-ray photoelectron spectroscopy and Kelvin probe force microscopy have demonstrated that the improvement in triboelectric output is correlated to molecular reorientation on the fibre surface caused by the applied voltage during electrospinning. The suitability of surface-modified electrospun fibres as high-performance materials for fibre-based triboelectric generators is demonstrated in this work, along with applications in intelligent textiles.


9:00 AM ES21.04.04
Triboelectric Technology Based Sensors for Human-Machine Interaction
Chenguo Hu; Chongqing University, Chongqing, China.

A sensing system is the core in human machine interaction (HMI), which connects the human being and machine with understanding the human instruction or senses. In this presentation, I will introduce the sensors based on triboelectric nanogenerator (TENG) technology, including an eye motion triggered self-powered mechanosensational communication system (1), a self-powered auditory sensor for social robotics and hearing aids (2), a quantization rotation sensing and gesture control of a robot joint (3), and a self-powered 2D barcode recognition system for personal identification. This work expresses notable advantages of using TENG technology to build a new generation of sensing systems for meeting the challenges in HMI.

References

9:30 AM ES21.04.05
Developing Energy Storage Devices for Nanogenerators as Small-Power Energy Harvesters
Xianmiao Lu; Beijing Institute of Nanoenergy & Nanosystems, Beijing, China.

Increasing demands for self-powered portable electronics and remote sensors have put forward imperative request on small power harvesting devices such as triboelectric nanogenerators that can collect environmental/ambient energy. Due to the intermittent nature of these power sources, energy storage for such devices is of significant importance for continuous power supply. When charged at low and intermittent power, energy storage devices such as supercapacitors or batteries need to handle pulse energy input and have minimal leakage current. However, research on energy storage devices with low self-discharge and high charging efficiency for small and pulse electric currents has not been paid enough attention. In this presentation, I will discuss our recent efforts in developing supercapacitors with suppressed self-discharge/improved frequency response that are suitable for small power harvesting applications.

For electric double layer capacitors (EDLCs), self-discharge has been an inevitable issue that causes decay of cell voltage and loss of stored energy. Due to self-discharge, applications of supercapacitors for long-term energy storage or collecting environmental energy harvested by small power devices have been severely limited. There are three main self-discharge processes for EDLCs, including i) charge diffusion and redistribution, ii) faradaic reactions, and iii) ohmic leakage. To alleviate this issue, we introduced an additive to the electrolyte to suppress the self-discharge of EDLCs. When the EDLCs are charged, the electric field in the double layers near the electrode surface induces much enhanced fluid viscosity. As a result, the diffusion of ions and redox species in the electrolyte can be impeded and the self-discharge rate can be reduced. We have demonstrated the decay rate of open circuit potential and leakage current can be reduced by more than 80%. Simulation results confirmed the reduced contribution of both diffusion of ions and faradaic reactions to the overall self-discharge. Furthermore, when the EDLCs were employed for storing energy harvested by a triboelectric nanogenerator (TENG) that has a characteristic of pulsed output current, much enhanced charging efficiency was attained. In another effort, we employed a low-cost charging material for the preparation of supercapacitors with high frequency response for pulsed charging. The high-frequency supercapacitors exhibited excellent frequency response with a phase angle of ~80° at 120 Hz. When the supercapacitors were employed for storing energy generated by a rotating TENG with pulsed output at frequencies ranging from 450 to 1350 Hz, the energy utilization efficiency was improved by more than 20% compared to conventional activated carbon based supercapacitors.

9:45 AM BREAK
The reliable production of atomically-thin crystals is essential for exploring new science and implementing novel technologies in the 2D limit. In this talk, I will discuss our recent discovery of a new 2-D material, tellurene, synthesized by a substrate-free solution process. The tellurene crystals exhibit process-tunable thicknesses from a monolayer to tens of nanometers, and lateral sizes ~ 100 µm. Our prototypical tellurene transistor device, which is air-stable, shows an excellent all-around figure of merits compared to existing 2D materials. We further carry out the first experimental exploration of piezotronic effect in tellurene and systematically investigate the piezotronic transport properties. The fundamental understanding of piezotronic coupling in tellurene is expected to provide insights for the development of 2-D material piezotronics, leading to the realization of “smarter” electronics for a multitude of emerging technologies, e.g., wearable electronics, soft robotics, medical prosthetics, and human-machine interface.


10:45 AM *ES21.05.02
Printing Two-Dimensional Piezoelectric Layers Using Liquid Metal Reaction Media
Nitu Syed1, Torben Daeneke2, Ali Zavabeti2 and Kourosh Kalantar-zadeh2; 1School of Chemical Engineering, University of New South Wales, Kensington, New South Wales, Australia; 2School of Engineering, RMIT University, Melbourne, Victoria, Australia.

The recent exploration of two dimensional (2D) planes as piezoelectric structures has accelerated. Mechanical displacements, such as vibration, bending and stretching, are ubiquitously present in the ambient environment and 2D structures may facilitate their sensing and the harvesting of their kinetic energy to power miniaturised devices based on such piezoelectric materials. Piezoelectric measurements using 2D materials, including their lateral strength and high crystallinity along the planes, large surface area to mass ratios and compatibility with surface fabrication processes, provide the concept of 2D piezoelectric with great prospect for future industries. Field of 2D piezoelectric materials can benefit from the emergence of crystals featuring high piezoelectric coefficients such as gallium phosphide (GaPO4). This 2D material is an archetypal piezoelectric with wide-ranging industrial applications. However, it does not naturally crystallise in a stratified structure and hence cannot be exfoliated using any of the conventional methods. Here we present a low temperature liquid metal 2D printing and synthesis strategy. Interfacial oxide layer of liquid gallium is exfoliated and surface-printed, followed by the vapour phase reaction between the gallium oxide sheet and phosphoric acid. The method gives access to large-area, uniform 2D GaPO4 nanosheets of unit cell thickness (~1.1 nm), while featuring wafer scale lateral dimensions. The unit cell thick nanosheet presents a large effective out-of-plane piezoelectric coefficient of nearly 8 pm/V. The developed liquid metal based process is also suitable for the synthesis of free-standing 2D GaPO4 nanosheets over micron sized cavities. The presented low temperature process is compatible with a variety of electronic device fabrication procedures, providing a facile route for the development of 2D piezoelectric devices for sensing and energy harvesting.

References:
method was used to fabricate PVDF, PVDF-barium titanate (PVDF-BT), PVDF-graphene, and PVDF-BT-graphene fibers. The volume fractions of BT and graphene were varied from 0.01 to 0.10, and a loom was used to weave the fibers into a fabric for testing. The properties of the textiles were measured before and after exposure to a contactless corona-discharge plasma to determine if additional pooling enhanced the performance of the fabrics. The piezoelectric strain coefficient, $d_{33}$, of the fabrics was measured using a piezometer at a frequency of 110 Hz. The impedance, resistance, conductance, and capacitance were measured using an impedance analyzer over frequency ranges of 20 Hz to 200 Hz and 20 Hz to 10 MHz. The geometric parameters of the textiles were also calculated to measure the resistivity, conductivity, and dielectric constant. The surface morphology of the textiles was analyzed with the aid of a scanning electron microscope.

SESSION ES21.06: Nanogenerators and Piezotronics I
Session Chairs: Christian Falconi and Rusen Yang
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 132 C

1:30 PM ES21.06.01
Piezo-Phototronic Effect Enhanced Photoelectrocatalysis Linlin Li; Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China.

TiO$_2$ is a well-known photocatalyst used for water splitting, pollutant removal, antibacterial application, etc. How to increase the efficiency by overcoming their limitation including fast recombination of photoexcited carriers, limited light utilization are still great challenge. In this talk, I will introduce our recent research progresses in piezo-phototronic effect enhanced photodynamic bacteria killing wound healing, and photoelectrocatalysis. For the first time, the tribo-layer of TENGs have been fabricated via dispersing the lead-free piezoelectric materials to increase the output performances, the fundamental mechanism of which is to enhance the triboelectric effect of materials mainly ferroelectric polymers. PVDF/PTFE based TENG. The enhancement in the performance of the TENG has been correlated with the changes in the properties of PVDF. We believe that this work will provide a simple yet effective way of enhancing the triboelectric effect of materials mainly ferroelectric polymers.

References

1:45 PM ES21.06.02
Structure Design and Enhancing the Performance by Dielectric Modulation of TENG for Harvesting the Blue Energy Yi Xi; Chongqing University, Chongqing, China.

Piezoelectric nanogenerator (TENG) has been considered to be a more effective technology to harvest various types of mechanic vibration energies such as wind energy, water energy in the blue energy and so on. Considering the vast energy from the blue oceans, harvesting of the water energy has attracted huge attention. There are two major types of "mechanical" water energy, water wave energy in random direction and water flow kinetic energy. Moreover, surface charge density of tribo-layer is the most key-point parameter for developing high performance TENG. Most of the previous works were focus on the surface structural/chemical modification, nevertheless the internal space of the tribo-layer and its mechanism exploration were less investigated. Herein, internal space charge zones are built through embedding ravines and gullies cross-cross gold layers in near-surface of tribo-layer, which leads to the high output performance of TENG. At the same time, the tribo-layer of TENGs have been fabricated via dispersing the lead-free piezoelectric materials to increase the output performances, the fundamental mechanism of the TENG has been discussed from the perspectives of dielectric modulation.

2:00 PM ES21.06.03
Unidirectionally Polarized Diphénylalanine Nanotube Based Piezoelectric Energy Generator Ju Hyuck Lee$^{1,2}$; *Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology, Daegu, Korea (the Republic of); *Bioengineering, University of California, Berkeley, Berkeley, California, United States.

Piezoelectricity is defined as the interconversion between mechanical and electrical energy induced by charge redistribution and separation when mechanical or electrical stimuli are applied to materials that do not have inversion symmetry. Although various conventional inorganic piezoelectric materials exhibit strong piezoelectric property, these materials often require substances that are harmful to the environment / human body or harmful to the environment during the fabrication process. Many natural biomaterials (eg, amino acid, peptide, protein, and virus) that can be synthesized in an environmentally friendly manner have been found to have piezoelectric properties and it is comparable to conventional piezoelectric materials. Recently, self-assembled diphénylalanine (FF) nanotubes have been reported to have strong piezoelectric properties comparable to conventional piezoelectric materials. However, the difficulty of fabricating unidirectionally polarized FF nanotubes that can convert mechanical forces into electrical energy has been a major impediment to the realization of high power bio-piezoelectric devices. Here, we develop a novel fabrication process to synthesize large-scale aligned and unipolarized FF nanotubes. We use a meniscus-driven self-assembly process which is environmental friendly process. By controlling the thermodynamic and kinetic parameters of fabrication process, we synthesized FF nanostructures ranging from vesicles to aligned peptide nanotubes. The resulting horizontally aligned FF nanotubes have unidirectional polarization. Furthermore, this synthesis process allows us to easily scale-up to form large-area coatings that we use to develop piezoelectric energy generator.

2:15 PM ES21.06.04
Enhanced Triboelectric Effect in PVDF—Changing Its Surface Roughness, Polarizability and Hydrophobicity Huidrom Hemojit Singh and Neeraj Khare; Indian Institute of Technology Delhi, Delhi, India.

With the advancement in technology and the urgent need for clean energy sources, triboelectric nanogenerator also known in short as TENG starts gaining lots of attention in recent years. TENG works on the principle of contact electrification, in which when two different materials come into contact charges are generated on the surface of the materials.$^{[1-3]}$ The amount of charges generated depend on various parameters, like surface roughness, work function, polarizability and hydrophobicity of the materials. $^{[4-6]}$

In the present work, we have modified surface roughness, hydrophobicity and polarizability of polyvinylidene fluoride (PVDF) by incorporating hydrothermally synthesized ZnO nanorods into PVDF. The changes in the above properties of PVDF lead to the enhanced triboelectric effect of PVDF. The films were prepared using a simple drop casting method, and no surface treatment or complex film synthesis techniques were not employed. TENGs fabricated by coupling ZnO-PVDF film with polytetrafluoroethylene (PTFE) showed a much enhanced triboelectric output of voltage of ~119 V and short circuit current of ~1.6 μA. The instantaneous output power is 65.6% more as compared to PVDF/PTFE based TENG. The enhancement in the performance of the TENG has been correlated with the changes in the properties of PVDF. We believe that this work will provide a simple yet effective way of enhancing the triboelectric effect of materials mainly ferroelectric polymers.

References
for the fabrication of high-quality ferroelectric devices and imply its role in a next-generation production of sensors, energy harvesters, and microelectromechanical systems.

Capacitors. The capacitors consist of lanthanum nickelate (LNO) electrodes and lead zirconium titanate (PZT) ferroelectric layer. To prepare the inks we first synthesized sol-gel precursor solutions and adjusted their physical properties by the addition of ethanolamine and ethylene glycol. The solvent composition was selected on the basis of our previous work to suppress the coffee stain formation of dried structures [A. Matavz et al., Appl. Phys. Lett. 113, 012904, 2018]. One of the most demanding issues in multilayer inkjet printing is the control over the wetting behavior throughout the fabrication process. To achieve this, we employed a few-nanometer-thick polymeric layer, which redefines the surface properties after each deposition step and ensures the repeatability during the fabrication of LNO/PZT/LNO stacks. The polymeric layer decomposes during annealing and does not influence the performance of capacitors.

Among them, a triboelectric nanogenerator (TENG), which is one of energy-harvesting devices, has been extensively investigated owing to several advantages such as cost-effectiveness, structural simplicity, wide material selection, and high conversion efficiency. Despite these attractive advantages, it remains a challenge to achieve a high output performance while preserving both the transparency and the flexibility because of the opaque and less flexible metal. Therefore, the triboelectric potential could be used to control the electrical transport in semiconductors. On the basis, several triboelectric functional devices have been developed including tribotronic smart skin, tactile sensing array and tuning diode, which has demonstrated triboelectricity-controlled electronics and established the active mechanosensation for external environment. In addition, the triboelectric power management strategy is also reviewed, in which the triboelectricity can be managed by electronics in reverse action. With the implantation of triboelectric power management module, the harvested triboelectricity by various kinds of human kinetic and environmental mechanical energy could be effectively managed as a power source for self-powered systems. According to the research prospects for interactions between triboelectricity and semiconductor, tribotronics is expected for significant impacts and potential applications in MEMS/NEMS; flexible electronics, robotics, wireless sensor network, and Internet of Things.

Flexible and Controllable Piezo-Phototronic Pressure Mapping Sensor Matrix by ZnO NW/p-Polymer LED Array Rongrong Bao and Caofeng Pan; Chinese Academy of Sciences, Beijing, China.

Flexible and Controllable Piezo-Phototronic Pressure Mapping Sensor Matrix by ZnO NW/p-Polymer LED Array. Functional tactile sensing device is mandatory for next-generation robotics and human-machine interfaces since the emulation of touching requires large-scale pressure sensor arrays with high-spatial resolution, high-sensitivity, and fast-response[11]. Some tactile sensors fabricated with organic transistors or micro-structured rubber layer pressure sensor arrays have been reported[12], whose working mechanism is based on changes in capacitance or resistance. Our group have demonstrated pressure sensor array base on piezotronic and piezo-phototronic effects. A spatial resolution of 120 µm was achieved for piezotronic pressure sensor array and an ultra-high resolution of 2.7 µm was derived from piezo-phototronic pressure sensor array using ZnO nanowire (NW)-p-GaN LEDs array[13]. These devices provide stable, fast response, as well as parallel-reading detections of spatial pressure distributions. However, the lacking of flexibility with a rigid sapphire substrate prevents the NW-LEDs array device from applications as smart skin; and the pressure measuring range of the device is in a relatively high pressure region. Therefore, a flexible pressure mapping system with moderate spatial-resolution become necessary and may find numerous potential applications in human-machine interfaces.

Organic/inorganic hybridized LEDs are drawing tremendous attentions because of their high flexibility. Among them, n-ZnO and p-poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate (PEDOT:PSS) hybridized inorganic/organic LED has aroused great technological and scientific interests due to the excellent optoelectronic properties of ZnO and the high flexibility, low-cost, easy fabrication, potential for large area deposition and commercial availability of PEDOT:PSS. Here, we demonstrate a flexible LED array composed of PEDOT:PSS and patterned ZnO NWs for mapping spatial pressure distributions. By utilizing strain-induced negative piezoelectric polarization charges presented at local interface of the p-n junction, piezo-phototronic effect has been applied to modify the band structure through reducing the barrier height for hole injections from PEDOT:PSS side, and thus facilitate the recombination between electrons and holes in ZnO side for enhancement of light emitting intensity. Therefore, the pressure distribution is obtained by parallel-reading the illumination intensities of LED pressure sensor array. The spatial resolution is achieved as high as 7 µm by fabricating ZnO nanowires on flexible substrate. By

Acknowledgement
This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education(2018R1A6A3A01011608).
controlling the growth conditions of the ZnO nanowire array, a wide range of pressure measurements from 40 MPa to 100 MPa are derived under different ZnO morphologies. For the CVD-grown large-area monolayer MoS\textsubscript{2}, we can see that the growth of the nanosheet is crucial for high-resolution stress sensors. Thus, we investigate the effect of sulfur treatment on the growth of the MoS\textsubscript{2} nanosheet.

**Reference**


**ES21.07.01 Piezo-Phototronic Effect Enhanced Performance of the Flexible Microwave Detectors**

Qianqian Du, Shuming Zhu, Jiandong Ye, Kun Tang, Youdou Zheng and Shulin Gu, Nanjing University, Nanjing, China.

Owing to the large surface to volume ratio and tunable surface morphologies, photodetectors based on low-dimensional nanostructures exhibit superior performance, thus many efforts have been made to optimize the photodetector devices [1]. Zinc oxide (ZnO) with the advantages of being flexible and fast and having high resolution in stress/pressure sensor applications, high chemical stability and outstanding optical properties in optoelectronics applications, has attracted significant attention in recent years[2]. In this study, the ZnO microwires were fabricated by a simple one-step chemical vapor deposition (CVD) method. We demonstrated photodetectors based ZnO microwires modified with NiO on a rigid SiO\textsubscript{2} substrate and the other on flexible polyethylene terephthalate (PET), respectively. We also investigated the electronic property of the devices with stress and light in detail. The results indicated that The piezo-phototopict effect can effectively enhance the performance of ZnO photodetector.

**Acknowledgment**

This research was supported by the National Natural Science Foundation of China (Nos. 61504057, 61574075, 61674077) and the Natural Science Foundation of Jiangsu Province (Nos. BK20150585).


**ES21.07.02 High-Performance Piezoelectric Nanogenerators Based on Composite Thin Films**

Su Yeon Lee, Eun Jung Lee, Sunho Jeong and Youngmin Choi; KRIST, Daejeon, Korea (the Republic of).

Energy harvesting that can scavenge various kinds of mechanical energy from several different sources has attracted great attention. In particular, a flexible energy-harvesting device consisting of piezoelectric materials has been studied and is regarded as a power source for flexible and wearable electronic devices because the piezoelectric elements can effectively convert to electrical energy from mechanical energy. Recently, many researchers have attempted to achieve highly efficient energy-harvesting devices using several fabrication methods. However, there are still the challenge problems with flexible piezoelectric nanogenerators. Here we report the flexible piezoelectric nanogenerators (PNGs) based on composite thin films comprising amine-functionalized lead zirconate titanate (PZT) nanoparticles (PZT-NH\textsubscript{3} NPs) and a thermoplastic triblock copolymer. Without additional dispersants, the uniform distribution of PZT-NH\textsubscript{3} NPs in the polymer composite improves the piezoelectric power generation compared to that of a PNG device using pristine PZT NPs. This unique composite behavior allows the PZT-NH\textsubscript{3} NP-based flexible PNG to exhibit a high output voltage of 65 V and current of 1.6 μA without time-dependent degradation. This alternating energy from the PNG can be used to charge a capacitor and operate light-emitting diodes through a full bridge rectifier. Furthermore, the proposed PNG is demonstrated as a promising energy harvester for potential applications in self-powered systems.

**ES21.07.03 Enhanced Piezoelectric Nanogenerator Performance by Point Defect Control of MoS\textsubscript{2}**

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The piezoelectric characteristics of two-dimensional materials are of great interest for high-performance piezoelectric potential applications. The CVD-based large-area monolayer MoS\textsubscript{2} is essential for practical applications. However, the CVD-based MoS\textsubscript{2} has the intrinsic defect of sulfur vacancies during the growth process, and these defects play an important role in screening the piezoelectric potential. So only small piezoelectric potential induced power output has been observed from the CVD-grown MoS\textsubscript{2}. Here we demonstrate a high performance piezoelectric nanogenerator using CVD-based monolayer MoS\textsubscript{2} nanosheet by an additional sulfur treatment process during the MoS\textsubscript{2} growth process. The measured piezoelectric coefficient (d\textsubscript{31}) of the CVD-grown large-area monolayer MoS\textsubscript{2} nanosheet is 3.73 pm V\textsuperscript{-1} using lateral PFM methods, and it generates a peak power density of 0.73 pW, which is 10 times higher than that of the pristine monolayer MoS\textsubscript{2} nanosheet.

**ES21.07.04 Nylon 11-MoS\textsubscript{2} Composite Layer with High Performance for Triboelectric Nanogenerator**

Minj Kim, Sol Lee, Anh Cao Viet, Daehoon Park and Junghyo Nah; Chungnam National University, Daejeon, Korea (the Republic of).

Triboelectric nanogenerators(TENGs) have gained much attention thanks to their relatively high output power through scavenging vibrating resources that exist in our living environment. To date, a number of approaches, such as surface patterning, dielectric permittivity modulation, chemical functionalization, have been introduced to enhance output performance of the TENGs. However, the TENG’s output performance has still been limited due to relatively low output current density on the triboelectric frictional surfaces. Therefore, simple and effective methods are necessary to boost the output current density of the TENG, which further extend the performance limit of the TENGs.
In this report, we adopted the composite structure consisting of MoS$_2$ flakes and ferroelectric Nylon 11 polymer to improve output current density. Here, ferroelectric Nylon 11 provides a knob to adjust surface triboelectric charge density by surface polarization. In addition, MoS$_2$ provides the trap states to further increase charge density in the composite structure. Using these two knobs, the output charge density was greatly improved in comparison to the TENG without the MoS$_2$ particles. Specifically, 5-fold higher current density was obtained by using the polarized MoS$_2$-Nylon 11 composite layer compared with the device fabricated only with non-polarized Nylon 11. Consequently, the maximum output power density of $-40$ mW/cm$^2$ was achieved in our work. The approach introduced here provides simple strategy to effectively extend the output performance limit of TENGs.

Acknowledgement: This subject is supported by Korea Ministry of Environment(MOE) as Advanced Technology Program for Environmental Industry Program.

**ES21.07.05**

**Role of Indium Zinc Oxide-Based Interfacial Layer for High Performance Triboelectric Nanogenerators**  
Dahoon Park, Kyung Soo Han, Sol Lee and Junghyo Nah;  
Chungnam National University, Daejeon, Korea (the Republic of).

Triboelectric nanogenerators (TENGs), which can effectively convert various mechanical stimuli to electricity by using a relatively simple device structure and cost-efficient, are considered as a promising candidate for coping with gradually increasing energy demands. To date, various research efforts have been reported to enhance the output performance of TENGs, which have greatly improved their output performance. However, triboelectric output performance enhancement is still hindered by its relatively low output current compared to its output voltage. Thus, further study is necessary to boost the output current density to further extend the performance limit of the TENG.  

In this work, we report the output performance enhancement method by inserting an indium zinc oxide (IZO) layer under polydimethylsiloxane (PDMS). Specifically, the 0.5 M IZO solution was prepared by spin-coating on stainless steel sheet, followed by curing and annealing processes. Next, IZO layer is buried by spin-coated PDMS. The TENG with a buried layer is relatively unaffected by surface wear-out. Furthermore, its output enhancement is considerably enhanced. The role of IZO layer is two folds: electron discharge from interface states at the IZO-PDMS interface and electron supply from the IZO layer by energy band bending during contact-separation motion. Consequently, the output performance of the TENG with an IZO layer is remarkably improved by adopting the IZO layer, generating an output power density of $-25$ mW/cm$^2$. Especially, about 9-fold increase of output current was observed in TENG with an IZO layer due to additional electron supplying effect by n-type semiconductor IZO. The approach presented here is a simple method for boosting the performance of TENGs and effectively alleviating their susceptibility to friction surface wear-out.

This research is supported by Korea Ministry of Environment(MOE) as Advanced Technology Program for Environmental Industry Program.

**ES21.07.06**

**A Novel Multi-Functional Self-Powered Pressure Sensor with Hierarchical Wrinkle Structure**  
Liming Miao, Hang Guo, Ji Wan, Haobing Wang, Xiaoliang Cheng and Haixia Zhang;  
Peking University, Beijing, China.

**Novelty:** This paper reports a novel multi-function self-powered pressure sensor with hierarchical wrinkle structure which is thin and flexible. Due to the sensitive hierarchical wrinkle structure, the sensor shows the sensitivity of 2.0 kPa$^{-1}$ and the excellent response performance of 0.15 ms (rise time) and 0.7 ms (relaxation time). In addition, the surface charges deriving from the contact of PDMS and ITO on the wrinkle structure enable the sensor to be a generator and differentiate various mechanical stimuli.

**Background:** With the development of electronic skins and wearable devices, flexible sensors based on capacitive effect due to its stability, are now concerned about by more and more people. One of the most of them require multi-features and complicated fabrication because of the complex designed dielectric layer. PDMS wrinkle structure fabricated by C$_4$F$_8$ plasma treating has been applied to triboelectric nanogenerator (TENG) and has the advantage of simple fabrication. However, the sensor with monolayer wrinkle structure shows low sensitivity. Here, we introduce hierarchical PDMS wrinkle structure into the capacitive effect pressure sensor to improve the performance of the sensor and meanwhile integrate the feature of energy harvesting.

**Fabrication Process:** The vacuum degassed mixture of PDMS base and cross-linker is spin coated on the indium tin oxide (ITO) coated polyethylene terephthalate (PET) film. Then heat the thin PDMS/ITO/PET film at 100 degree celsius for 45 seconds. Next implement a C$_4$F$_8$ plasma treatment for 1000 seconds, after which the heat the film till the curing of the thin PDMS layer. Finally, cover the wrinkle-structured film with another ITO/PET film. The thickness and area of the sensor are about 260 μm and 6.25 cm$^2$, respectively.  

**Working principle:** As a capacitive effect sensor, the ITO layers work as two conductive electrodes and the dual-scale wrinkle structure, the thin PDMS layer and the air work as dielectric layer. While as a generator, the PDMS and ITO work as charges generation surface and the air between the wrinkle gap enables PDMS layer and ITO layer to contact and separate. The hierarchical wrinkle structure manages differentiating normal pressure and bending.

**Experimental Results:** Since extending C$_4$F$_8$ plasma treating time to 1000s can produce hierarchical wrinkle structure on the PDMS surface, the sensitivity in the relatively low pressure regime (0-500 Pa) can get an obvious promotion from 0.5 kPa$^{-1}$ (50s plasma treating), 1.0 kPa$^{-1}$ (500s plasma treating) to 2.0 kPa$^{-1}$ (1000s plasma treating). Moreover, in the relatively high pressure regime (more than 1500 Pa), the sensitivity of the sensor gets a slight promotion from 0.1 kPa$^{-1}$ (50s & 500s plasma treating time) to 0.2 kPa$^{-1}$ (1000s plasma treating time). Moreover, the response performance is excellent with the release-time is 0.7 ms and the rise-time is even only 0.15 ms. When pressure is applied, the small wrinkle firstly works and then sense the pressure quickly and sensitively by forming deformation, thus the sensitivity of the pressure sensor in the relatively low pressure regime can be highly enhanced and the response time is extremely short. When the pressure is applied extremely high, the big wrinkle begins to work and shows a sensitivity of 0.2kPa$^{-1}$ once bigger than that of a PDMS plate. As a TENG, the output voltage of the sensor under bending stimuli is about 300 mV, while that of the sensor under pressure stimuli is only about 75 V. The output current of the former is about 3μA, while the latter is about 17 μA. The wave pattern under pressure stimuli is more sharp than that under bending stimuli. The reason for the feature of mechanical stimuli differentiation of the device can be attributed to the hierarchical wrinkle structure. The two forces can make hierarchical wrinkles contact with the PET/ITO with different deformation which leads to different contact area thus results in output voltage and current.

**ES21.07.07**

**Helicene-Based Polymers** Joshua C. Sevlar and Ruel McKenzie; Polymer Engineering, University of Akron, Akron, Ohio, United States.

**Helicenes** are a unique group of helically configured aromatic compounds which have been shown to possess potentially useful properties. Pertinent to this proposed research, helicenes have been shown both computationally and experimentally to be piezoelectric. It is the intent of this research to show how to utilize functionalized helicenes as monomers in the backbone of existing polymer systems. In this way, a new multi-functional class of polymers will be developed which possess the inherent properties of helicenes. These molecules derive their piezoelectric properties from the inherent strain in the molecule originating from their helical shape. This is unlike existing piezoelectric polymers such as poly-(vinylidene fluoride) (PVDF) whose piezoelectric properties originate from interaction between dipoles in the polymer structure. This research will begin with the synthesis of a diol-functionalized, nine-ringed helicene for application in a proof-of-concept polyester system. Initial characterization of this polymer will provide insight the as-synthesized properties of this novel polymer, and later optimization of piezoelectric properties will show the presence and extent of the functional activity of the polymer. The capability of these molecules to be adapted for use in various polymer chemistries give this new class of polymers potential for use in applications where material properties have previously limited the versatility of piezoelectric polymers.

**ES21.07.08**

**Localized Plasmon-Stimulated Triboelectric Nanogenerator**  
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We report for increase the surface charge density of the TENG using a surface plasma resonance. Resonant energy transfer (RET) generates electron–hole pairs in the thin PDMS layer and the air work as dielectric layer. While as a generator, the PDMS and ITO work as charges generation surface and the air between the wrinkle gap enables PDMS layer and ITO layer to contact and separate. The hierarchical wrinkle structure manages differentiating normal pressure and bending.

**Experimental Results:** Since extending C$_4$F$_8$ plasma treating time to 1000s can produce hierarchical wrinkle structure on the PDMS surface, the sensitivity in the relatively low pressure regime (0-500 Pa) can get an obvious promotion from 0.5 kPa$^{-1}$ (50s plasma treating), 1.0 kPa$^{-1}$ (500s plasma treating) to 2.0 kPa$^{-1}$ (1000s plasma treating). Moreover, in the relatively high pressure regime (more than 1500 Pa), the sensitivity of the sensor gets a slight promotion from 0.1 kPa$^{-1}$ (50s & 500s plasma treating time) to 0.2 kPa$^{-1}$ (1000s plasma treating time). Moreover, the response performance is excellent with the release-time is 0.7 ms and the rise-time is even only 0.15 ms. When pressure is applied, the small wrinkle firstly works and then sense the pressure quickly and sensitively by forming deformation, thus the sensitivity of the pressure sensor in the relatively low pressure regime can be highly enhanced and the response time is extremely short. When the pressure is applied extremely high, the big wrinkle begins to work and shows a sensitivity of 0.2kPa$^{-1}$ once bigger than that of a PDMS plate. As a TENG, the output voltage of the sensor under bending stimuli is about 300 mV, while that of the sensor under pressure stimuli is only about 75 V. The output current of the former is about 3μA, while the latter is about 17 μA. The wave pattern under pressure stimuli is more sharp than that under bending stimuli. The reason for the feature of mechanical stimuli differentiation of the device can be attributed to the hierarchical wrinkle structure. The two forces can make hierarchical wrinkles contact with the PET/ITO with different deformation which leads to different contact area thus results in output voltage and current.

**ES21.07.09**

**Tunable Tribolectric Dual-Gate Logic Devices Based on 2D MoS$_2$ and Black Phosphorus**  
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2University of Chinese Academy of Science, Beijing, China.

With the Moore’s law hitting the bottleneck of scaling-down in size (below 10nm), personalized and multifunctional electronics with an integration of two-dimensional (2D) materials and self-powering technology emerges as a new direction of scientific research. Triboelectric nanogenerators (TENGs) that efficiently convert mechanical energy into...
electric power have great potential in self-powered smart systems and modulating semiconductor devices. As the basic components in integrated circuit, logic circuits based on 2D materials transistors have a promising potential. Here, we report a tunable tritobronic dual-gate logic device based on MoS2-FET, black phosphorus FET and a sliding mode TENG. Triboelectric potential produced from the sliding mode TENG under an external displacement can efficiently drive the complementary transistors and logic devices without applying a gate voltage. The high-s top gate dielectrics contributes to the increase of the effective capacitance of the device, leading to high performance tritobronic transistors with on/off ratio exceeding 10^4 and cutoff current below 1 pA/μm, which are the best ever obtained. Tunable electron behaviors of the logic device are also achieved according to different displacements of TENG coupled to the bottom gate, including tunable gains (improved to be ~13.8) and power consumptions (~1 nW). This work offers a low-power-consuming, active and a general approach to modulate semiconductor devices and logic circuits based on 2D materials with TENG, which can be used in micro-electromechanical systems, human–machine interfacing, data processing and transmission.

ES21.07.10
An Ambitious Triboelectric Nanogenerator for Multi-Environmental Smart Monitoring
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With the advancement of human science and technology and the improvement of living standards, more people begin to put forward higher requirements for environmental conditions. Traditional and non-intelligent monitoring devices are gradually being replaced by intelligent, self-driven, simple in structure, and low-cost environmental monitoring systems, such as triboelectric nanogenerators. We report a triboelectric nanogenerator based on a tumbler structure, which adapts to the complex environment of amphibious, moisture and repeated impact, and can simultaneously collect water and wind energy in any direction and low frequency. A single device can achieve an output voltage to 140V and short-circuit current to 0.5μA. It can not only monitor wave height and wave frequency on the ocean, but also a wide range of wind speeds, even a breeze on land. Moreover, swimming pool water quality can be detected through the residual chlorine index. The advantage lies in adapting to the amphibious environment and reflecting on low frequency and irregular disturbances, with good prospect applications in the environmental monitoring field.

ES21.07.11
High Voltage Output Contact-Separation Mode Triboelectric Nanogenerators Based on Commercial-Available Polymers
Micky Wong; Hong Kong Polytechnic Univ, Hong Kong, Hong Kong.

As a sustainable power source, triboelectric nanogenerators (TENGs) have attracted extensive attention from both academia and industry to solve the growing energy crisis. Herein, a high voltage output contact-separation mode triboelectric nanogenerator is demonstrated by using commercial-available polyurethane foam and ebonite as triboelectric materials, which presents flexibility, durability and reliability, simultaneously. The dependence of electric outputs on the different parameters of the TENGs, including triboelectric affinity, gap distance between frictional layers, and the dimension of devices, has been systematically investigated. The optimized device can generate an open-circuit voltage of above 1000 V and a short-circuit current of above 100 μA. The TENG can operate continuously for 500 k cycles under large pressuring force with stable output performance. Meanwhile it can harvest mechanical energy from various human motions, such as stepping and tapping. Arising from its reliable high voltage output, the device can be utilized as a self-powered spark plug. This study provides a feasible method for developing power sources in simple fabrication and low-cost way. The work was supported by the grant of Research Grants Council of Hong Kong.

ES21.07.12
Vibration Based Piezoelectric-Electromagnetic Hybrid Energy Harvester for Autonomous Sensor Systems
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With the advent of the IoT era, the demand for sensors has increased significantly. We note that these sensor systems can communicate with each other over wireless networks in the IoT era. Especially, in particular sites where access to power is difficult, batteries have been installed as power source for wireless sensor systems. However, these batteries have a limited lifetime and require periodic replacement. So, various energy harvesting technologies have received research attention to realize an autonomous wireless sensor network by replacing the batteries. Due to relatively low power generation capability and energy conversion efficiency, however, these harvesting technologies have been applied only to limited applications.

In order to address these issues, here, we design and demonstrate a piezoelectric/electromagnetic hybrid energy harvester that can generate significant amount of electricity at vibration environments(Fig 1). Oval-like configuration using two curved piezoelectric energy harvesters based on MFC(Macro-fiber composite) piezoelectric material induces large displacement of a permanent magnet installed at the end of the top surface which allows efficient power generation both piezoelectric and electromagnetic energy harvesters. Compared to output average power (1.09 mW) of cantilever type piezoelectric energy harvester, piezoelectric part of Oval-shaped harvester shows about two times higher output average power (2.58 mW) at 0.5 g and 60 Hz vibration due to its enhanced vibration characteristics. Also, we provide the resonance frequency tuning guidelines and the optimization strategies of the Oval-shaped hybrid energy harvester using Finite Element Analysis (FEA) and mechanical equivalent system. The hybrid energy harvester contains two magnets facing same polarity on both side of Oval-shaped monolith. This configuration improves the spring constant of Oval-shaped harvester, reducing the damping ratio, efficiently. With two magnets, the Oval-shaped hybrid energy harvester with MFC achieves up to 1.03 mm displacement at 60 Hz and 0.5 g vibration conditions. Also, considerable improvement of output power is observed at both piezoelectric and electromagnetic parts. The output average power of piezoelectric part and electromagnetic part are 7.66 mW (239.4 μW/cm^2) and 0.60 mW (18.8 μW/cm^2), respectively. Total hybrid output power is 8.26 mW which is sufficient power for operating commercialized Bluetooth module (5 mW), continuously. This milliwatt-scale (~mW) hybrid energy harvester provides us the opportunity to realize autonomous sensor system to come in the near future.

ES21.07.13
Tuning the Photoluminescence of Aggregation-Induced Emission Luminogens via Magnetostrictive Stress and Piezoelectric Strain
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Many aggregation-induced emission (AIE) luminogens exhibit mechanochromic effect through grinding the luminogen powdery. The AIE luminogens undergo bright-dark switching between crystalline and amorphous states. However, a relatively high pressure is required to trigger the phase transfer. Meanwhile, the color manipulation cannot be realized in an in situ and reversible manner, which limits some of their applications. Smart materials including piezoelectrics and magnetostricrion materials provide the opportunities to couple external field to the AIE materials and realize more flexible controllable AIE. In this work, magnetic alloy nanoparticles iron cobalt nickel and piezoelectric poly(vinylidene fluoride) (PVDF) have been utilized to tune two kinds of aggregation-induced emission luminogens. Precise control over the emission intensity of luminogens under the external applied magnetic field or electric field has been demonstrated. The AIE has been decreased with the magnetostricative stress increasing, which is contributed to the looser molecular structure of AIE luminogens under the stimulating of a time-varying magnetic field. While, the piezoelectric strain induced an enhancement of emission intensity under electric field, which originates from the contact of PVDF lattice constant and restriction of intramolecular rotations of AIE luminogens. Thus, these results are expected to enrich the understanding of the luminescence process of AIE luminogens and promise more flexibility of AIE luminogens for the magnetic-optical and optoelectronic applications.

ES21.07.14
Growth and Characterization of Spatially-Ordered PZT Nanostructures by Glancing Angle Pulsed Laser Deposition
Domingo Mateo-Feliciano, Derick DeTelleml, Pritish Mukherjee and Sarahh Wittamichi; University of South Florida, Tampa, Florida, United States.

Lead Zirconium Titanate (PZT) is one of the most widely used piezoelectric materials due to its high piezoelectric constant, great piezoelectric response, operating temperature relative to other used piezoelectrics and is one of the industry standard materials in DRAMS and MEMs due to its ferroelectric properties. In addition, PZT is of great interest in piezotronics applications but achieving spatially ordered arrays are a challenge for device construction. This paper presents the characteristics of hexagonal closed-pack PZT nanocolumns grown by a Glancing Angle Pulsed Laser Deposition (GAPLD) technique on a template silicon (Si) substrates. The substrate is patterned with a self-assembled monolayer of Silica Nanospheres (SNs) of sphere sizes of 3.5 μm, 1.18 μm, 850 nm, 500 nm, 250 nm and 150 nm in diameter by Langmuir-Blodgett technique. Subsequently, PZT was deposited by GAPLD technique at an oblique angle to the substrate to promote ballistic shadowing. In this study, we pursued an investigation of the columnar angle’s
relationship with the deposition angle, and its effect on the crystallinity of the PZT nanostructured films. Results pertaining to the morphology, structure, and composition investigated for varying template sizes by SEM, EDS, AFM, and XRD will be presented.

**ES21.07.15**

**Mechanically Stable ZnO Hexagonal Nanopyramids Array for High Performance Piezoelectric Applications**

Jeongmin Lim and Alfredo A. Martinez-Morales
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Mechanical force-driven power generation can be achieved by the utilization of piezoelectric materials that produce electricity in response to external mechanical stress. Diverse piezoelectric crystal structures such as perovskite and wurtzite have been studied for piezoelectric nanogenerator applications. In particular, ZnO is extensively researched due to its semiconducting properties, along with its directional preferential crystal growth nature. The piezoelectric materials of ZnO have been demonstrated mostly through the bending stress of one-dimensional nanostructures such as nanowires. The utilization of ZnO in piezoelectric applications can be significantly improved by using the piezoelectric operation mode δ33, via the structural engineering (morphology) of crystalline ZnO from one-dimensional to pyramidal nanostructures.

In this work, our modified CVD synthesis technique is applied to synthesize the mechanically stable and highly piezoelectric ZnO hexagonal nanopyramids array. The superior mechanical stability was achieved through the morphology engineering of ZnO as a step-wise pyramidal structure. The single crystal pyramidal ZnO was grown in vertically-aligned pyramidal structures by controlling the supply of Zn vapor precursor during synthesis. The piezoelectric performance was measured by piezoelectric force microscopy under the highest piezoelectric operation mode δ33. The piezoelectric performance was improved by increasing the crystallinity and reducing planar and point crystal defects, as confirmed by transmission electron microscopy and X-ray diffraction analysis. The mechanical, optical, and physical characteristics of synthesized ZnO nanopyramids were characterized by piezoelectric force microscopy, photoluminescence spectroscopy, and Raman spectroscopy.

**ES21.07.16**

**Ultrasensitive Triboelectric Nanogenerator for Weak Ambient Energy**

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Higher requirements have been put forward for self-powered systems operated with weak energy in the environment. Sensitivity, efficiency and power management design of the energy harvesting module play key roles on the sustainability of the system. In this work, we present an ultrasensitive triboelectric nanogenerator (TENG) with Cu coated fluorinated ethylene propylene films stacked in a unipolar manner and suspended by springs. Triboelectricitization and electrostatic induction take place between every adjacent film surfaces, during which transferred charges are increased by at least 50%, leading to an increased efficiency. Also, the reduced framework weight makes soft spring can be adopted for greatly improved sensitivity. Depending on the investigation of mechanical motion in the system, TENG’s energy harvesting efficiency is boosted by bringing down the moment of inertia. The linear region characteristic of an n-type junction field-effect transistor is utilized for a low-loss power management design with greatly reduced power consumption and start-up time for superior weak energy harvesting applications. Ultrasensitive and high efficient energy harvester with low-loss power management demonstrated in this work promises an outlook for an effective approach to achieve more powerful and more sustainable self-powered systems working with comprehensive ambient weak mechanical energy fitted in diverse application circumstances.

**ES21.07.17**

**Piezoelectric Effect Tuning on ZnO Microwire WGM Lasing**

Junfeng Lu, Caofeng Pan and Zhong Lin Wang; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

Piezoelectric force microscopy, photoluminescence spectroscopy, and Raman spectroscopy.

Laser has higher applications in science and technology, from medical to manufacture and to defense. An important characteristic of a laser is its wavelength and width of wavelengths. Wavelength tunable nanolasers are promising for multifunctional applications in all-optical integrated nanodevices, optical communication, optical sensing technology and spectroscopy analysis. However, most of the methods for tuning the lasing modes are lack of a dynamical tenability, that is, the ability to reversibly modulate the stimulated emission in a pre-prepared single micro/nanodevice.

In this work, a novel method for a dynamic tuning on coherent light emission wavelengths of single ZnO microcavity has been proposed. Owing to the dominant role occupied by the piezoelectric polarization effect in the wurtzite-structure ZnO microwre, the effective dielectric constant (or refraction index) of the gain media is modulated towards an increasing trend by applying a tensile strain, resulting in a shift of the strain-mediated whispering-gallery mode (WGM) lasing at room temperature. Due to the narrow linewidth in the lasing mode, the strain-dependent spectral resolution is improved by an order of magnitude, making it feasible for achieving high-precision, ultra-sensitive and non-contact stress sensing. Our results have an important impact on laser modulation, optical communication and optical sensing technology.

**References**


**ES21.07.18**

**Biodegradable Triboelectric Nanogenerator for Biomedical Devices**

Qiang Zheng and Zhou Li; Chinese Academy of Sciences, Beijing, China.

Over the last 60 years, implantable electronic systems and devices have undergone a significant transformation, becoming a valuable biomedical tool for monitoring, measuring and soliciting physiological responses in vivo. Where in vivo sensing or stimulation is required for a short period of time, degradable implantable electronic devices can provide a solution to overcome inflammation and infections associated with long-term implant utilization. Moreover, subsequent surgical removal of these devices can be avoided which will diminish the pain and cost to the patient. Currently, fabricating a complex high-performing electronic system from entirely biodegradable, non-toxic set of electronic materials is of growing interests. However, a reliable electrical power source that suitable for those transient implantable electronic devices still has not been experimentally investigated previously.

We demonstrated a set of materials, manufacturing schemes, device components for a biodegradable triboelectric nanogenerator (BD-TENG) which can harvesting mechanical energy in vivo and physically disappeared at prescribed times without any adverse long-term effects.

Tunable electrical output capabilities and degradation features were achieved by fabricated BD-TENG using different materials. When applying BD-TENG to power two complementary micro-grating electrodes, DC pulsed electrical field was generated and the neural cell growth was successfully orientated, showing its feasibility for in-vivo neuron repairing.

Our work demonstrates a significant potential of BD-TENG as a power source for transient implantable medical devices.
Laser Diodes Due to Piezo-Photonic Effect
Redefinition the Quasi-Fermi Energy Levels Separation of Electrons and Holes Inside and Outside Quantum Wells of GaN Based Multi-Quantum-Well Semiconductor

photocurrent and also provide a potential way to optimize the performance of self-powered PDs. The phototronic effect on the transient and steady-state photocurrent are revealed based on the bandgap diagrams. The results may help us to further clarify the mechanism of the pyro-electric effect relative to that obtained from the steady-state signal. The relative persistent secondary pyroelectric effect weakens the height of Schottky barrier, leading to a reduction of the electric potential distribution during device operation. The MENG sensor exhibited a stable open circuit voltage of 10.2 V at a 30.8 kPa pressure and a calculated sensitivity of 331 mV/kPa. The stability testing result showed that the device has only ~ 5% attenuation after 10,000 cycles of repeated testing at 30.8 kPa pressure. Furthermore, it was found that the MENG sensor responds not only to a dynamic force but also a static force. Finally, a sensor array consisting of nine MENG sensor elements was fabricated. The testing results from the sensor array also revealed that a single touch of the sensor element can immediately light up an LED light at the corresponding position. This device holds great promise for use in future tactile sensors and artificial skin applications.

A Monocharged Electret Nanogenerator-Based Self-Powered Device for Pressure and Tactile Sensor Applications Shaobo Gong, Jinxi Zhang, Chenchen Wang and Kaijiang Ren; Beijing Institute of NANOenergy and Nanosystems, Beijing, China.

This study reports a self-powered pressure sensor based on a monocharged electret nanogenerator (MENG). The sensor exhibits great advantages in terms of high reliability, ease of fabrication, and relatively high sensitivity. The working mechanism of the MENG sensor was studied by both theoretical derivations and finite element analyses to determine the electric potential distribution during device operation. The MENG sensor exhibited a stable open circuit voltage of 10.2 V at a 30.8 kPa pressure and a calculated sensitivity of 331 mV/kPa. The stability testing result showed that the device has only ~ 5% attenuation after 10,000 cycles of repeated testing at 30.8 kPa pressure. Furthermore, it was found that the MENG sensor responds not only to a dynamic force but also a static force. Finally, a sensor array consisting of nine MENG sensor elements was fabricated. The testing results from the sensor array also revealed that a single touch of the sensor element can immediately light up an LED light at the corresponding position. This device holds great promise for use in future tactile sensors and artificial skin applications.

Integrated Rotating Triboelectric Nanogenerator with Wireless Energy Delivery for Smart Home Yang Jie¹, Jinjing Ma², Yandong Chen¹, Ning Wang², Zhong Lin Wang² and Xia Cao³; Beijing Institute of NANOenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China; University of Science and Technology Beijing, Beijing, China.

Both energy harvesting and power delivery are the key technology for self-powered systems, so the organic integration of two technologies can improve the performance. Herein, we develop an integrated rotating triboelectric nanogenerator (TENG) based on Maxwell’s displacement current to collect ambient rotational energy for wireless energy delivery (WED). To avoid the defects of continuing friction, a new disconnect-type TENG with the simple structure of four sectors is designed. By matching with the collectors at the vertical height of 2 cm, the output of WED has the rectified current and voltage of ~3 μA and ~17 V. And small mobile electronics can be powered without wires due to the maximum value of ~22 mW m⁻². Besides, a contact-type TENG is integrated with the disconnect-type TENG to improve the efficiency and adaptation. The mobile phone and digital camera can be charged by the contact-type TENG with an electrical output of ~2 mA and ~110 V. This work shows a new prototype of hybrid TENG with WED, which makes it feasible and convenient for the electric power supply in smart home.

Effective Wound Healing Enabled by Wearable Triboelectric Nanogenerator Yin Long, Hao Wei, Jun Li, Guang Yao, Weibo Cai, Angela L. Gibson and Xudong Wang; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Non-healing skin wounds affect more than 6.5 million people in the United States, and result in enormous health care expenditures and long-term physical and mental suffering. Most of current strategies, including wound debridement, compression bandaging, wound dressing, hyperbaric oxygen therapy, negative pressure therapy, and ultrasonography, are passive treatments and rarely participate in controlling endogenous cell behaviors. Electrical stimulation (ES), which imitates the natural wound healing mechanism of the endogenous electric field to facilitate skin growth, is an attractive adjunct to wound care and has a potential to treat many different types of acute and chronic skin wounds with minimal adverse effects and good simplicity to apply.

The recent innovation of triboelectric nanogenerator (TENG) opened a new route for generating periodic biphasic electric pulses by locally converting mechanical displacements, such as body or muscle motions. This exceptional capability makes TENG a unique candidate for producing electrical stimulations that is self-sustainable and biologically responsive. Besides, TENGs could be made flexible with reasonably high output power density and energy conversion efficiency. Here we report an efficient electrical bandage for accelerated skin wound healing. On the bandage, an alternating discrete electric field is generated by a wearable nanogenerator by converting mechanical displacement from skin movements into electricity. Rat studies demonstrated rapid closure of a full-thickness rectangular skin wound within 3 days as compared to 12 days of usual contraction-based healing processes in rodents. From in vitro studies, the accelerated skin wound healing was attributed to the electric field-facilitated fibroblast migration, proliferation and transdifferentiation. This self-powered electric-dressing modality could lead to a new and facile therapeutic strategy for non-healing skin wounds treatment.

Comprehensive Pyro-Phototronic Effect Enhanced Ultraviolet Detector with ZnO/Ag Schottky Junction Laijun Zhu and Zhong Lin Wang; Chinese Academy of Sciences, Beijing, China.

As a coupling effect of pyroelectric and photoelectric effect, pyro-phototronic effect has demonstrated an excellent tuning role for fast response p-n junction photodetectors (PDs). Here, a comprehensive pyro-phototronic effect is utilized to design and fabricate a self-powered and flexible ultraviolet PD based on the ZnO/Ag Schottky junction. By using the primary pyroelectric effect, the maximal transient photocurrent sensitivity of the self-powered PDs can reach up to 1.25 mA W⁻¹ for 325 nm illumination, which is improved by 1465% relative to that obtained from the steady-state signal. The relative persistent secondary pyroelectric effect weakens the height of Schottky barrier, leading to a reduction of the steady-state photocurrent with an increase in the power density. When the power density is large enough, the steady-state photocurrent turns into a reverse direction. The corresponding tuning mechanisms of the comprehensive pyro-phototronic effect on transient and steady-state photocurrent are revealed based on the bandgap diagrams. The results may help us to further clarify the mechanism of the pyro-phototronic effect on the photocurrent and also provide a potential way to optimize the performance of self-powered PDs.

Redefinition the Quasi-Fermi Energy Levels Separation of Electrons and Holes Inside and Outside Quantum Wells of GaN Based Multi-Quantum-Well Semiconductor Laser Diodes Due to Piezo-Phototronic Effect Dinge Li¹, Lifeng Feng², Wei Yang¹, Xiaodong Hu¹ and Cundu Wang²; Chinese Academy of Sciences, Beijing, China; Tianjin University, Tianjin, China; Peking University, Beijing, China.

Both accurate experiments and a self-consistent theoretical simulation using the near-ABC or ab initio method have uncovered the anomalous changes in the junction voltage (Vj) of GaN-based lasers. Here, further accurate emission spectrum characteristics and band-gap simulation of a GaN based laser diodes (LDs) confirmed that previous researchers may have been confused the junction voltage (Vj) of LDs and the separation in the two Fermi levels of electrons and holes in the active region divided by the electronic charge. For the multiple-quantum wells (MQWs), there are obvious differences between them due to piezo-photonic effect. For the ideal GaN-based LDs, despite the increase in junction voltage, physical quantities including the separation between the two Fermi levels of electrons and holes in the MQW region, the optical net gain, the carrier concentration have remained unchanged beyond the threshold region after an unpredictable sharp increase in the threshold region.

Efficient Piezocatalytic Activity Driven by the Piezoelectric Effect of BaTiO₃ Nanowires Jue Wang, Ni Qin and Dinghua Bao; Sun Yat-Sen University, Guangzhou, China.

Recently, a novel catalysis technology, which named piezocatalysis, has received significant attention due to independence of light irradiation. Here, we report the new advances in the piezocatalysis of BaTiO₃ and further investigate the relationship between piezoelectric potential and piezocatalysis. In this work, we successfully synthesized...
BaTiO$_3$ nanowires and nanoparticles by a two-step hydrothermal method. It was found that the BaTiO$_3$ nanowires exhibit effectively enhanced piezocatalytic activity under ultrasonic vibration compared with the BaTiO$_3$ nanoparticle. To explore the origin of the excellent piezocatalysis performance of BaTiO$_3$ nanowires, the distribution of piezoelectric potential in these nanomaterials was simulated by the finite element method (FEM) with the aid of COMSOL multiphysics software package. On the basis of the piezoelectric potential analysis by FEM simulation, the enhanced piezocatalytic activity of the BaTiO$_3$ nanowires can be attributed to the larger piezoelectric potential along the polar axis. A relatively larger piezoelectric potential of the catalyst surface can induce a greater shift of conduction band and valence band, resulting in easier and faster immigration of the electrons and holes, during reacting with dissolved oxygen and hydroxyl to form superoxide radicals and hydroxyl radicals. Furthermore, we demonstrate that the intrinsic charge carriers (not piezoelectric charges) in piezoelectric crystallites play the role of charge transfer in the catalysis process through regulating the concentration of charge carriers in catalyst. This study provides further understanding piezocatalysis of piezoelectric nano-materials as well as insights on the relationship between piezoelectric potential and piezocatalysis.

ES21.07.27
Multimodal Enhancement of Luminescent Light Harvester And Triboelectric Touch Sensor via P(VDF-TrFE) Hong Joon Yoon and Sang-Woo Kim; Sungkyunkwan University, Suwon, Korea (the Republic of).

Display technology has not only presented information traditionall but also multifunctional capability, flexibility, lightness and slimmness design are desired attributes for being adopted by artificial intelligent (AI) to interact with consumers. In this regard, ferroelectric poly(vinylidenefluoride-co-trifluoroethylene) (PVDF-TrFE) is of great interest as potentially applicable for display power saving material with having mechanical stability, transparency, and electrically controllable polarization. Here, we report the experimental study of a luminescent light harvesting property of CdSe QD embedded P(VDF-TrFE) nanocomposite, whereas the concentration of QD is not as much high as to interfere presenting information in visual. In agreement with theoretical calculation, the converted power from luminescent light guided to the c-Si solar cell is enhanced by 42% based on the quantum-confined Stark effect (QCSE) owing to ferroelectric polarization of P(VDF-TrFE). The resulting nanocomposite shows enhanced mechanical sensitivity (~40%) by aligned dipole moment of P(VDF-TrFE) upon mechanical contact. This nanocomposite material may potentially be applicable as multimodal display element not only enable to power itself but also detect given mechanical touch.

ES21.07.28
Butylated Melamine Formaldehyde and CaCu$_2$TiO$_4$: Particles Based Composite Dielectric Layer for High Output Performance Triboelectric Nanogenerators Jinwo Kim and Sang-Woo Kim; Sungkyunkwan University, Suwon, Korea (the Republic of).

Triboelectric nanogenerators (TENGs) offer a promising approach for mechanical energy harvesting, but an effective strategy for enhancing the output performance is a crucial requirement. Though many studies have been performed to maximize the triboelectric effect on the surface of dielectric materials, studies for improving electrostatic induction phenomenon inside the dielectric materials have not yet been conducted. Here, we propose a high output performance TENG with a composite of butylated melamine formaldehyde (BMF) matrix and the high dielectric constant particles of CaCu$_2$TiO$_4$ (CCTO) as an excellent dielectric layer for enhancing the electrostatic induction phenomenon. The high dielectric constant CCTO particles result into a strong polarization of the dielectric materials under the triboelectric field. As a consequence, the charge induction in the bottom electrode is enhanced thereby increasing the triboelectric output power. A rotation-type freestanding mode TENG based on BMF-CCTO 1wt% composite has produced an RMS voltage and a current density (268 V and 25.8 mA/m$^2$) which is about 3 times higher than that (113.2 V and 8.7 mA/m$^2$) of the TENG based on pure BMF. The strategy of incorporating the high dielectric constant CCTO particles is completely general and can be applied to any polymer matrix in order to enhance the output performance of TENGs.

ES21.07.29
In Situ TEM Investigation of Stress-Induced Recoverable Charged Domain Walls in Barium Titanate Qianwei Huang$^{1}$, Zibin Chen$^{1}$, Feifei Wang$^{2}$, Yu-Wing Mai$^{3}$, Simon Ringer$^{4}$, Haosu Luo$^{5}$ and Xiaozhou Liao$^{6}$; $^{1}$The University of Sydney, Sydney, New South Wales, Australia; $^{2}$Shanghai Normal University, Shanghai, China; $^{3}$Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Domain walls in ferroelectric materials act as functionalized interfaces. The atomic structures in domain wall areas have a significant impact on the properties of the domain walls. Both theoretical simulations and experimental measurements demonstrated that dense charged domain walls (CDWs) can effectively enhance the piezoelectric response of ferroelectrics. Usually CDWs do not steadily exist due to the high electrostatic energy. In some cases, the formation of CDWs can be realized via electrical bias. However, applying an electric field to ferroelectrics could induce current leakage. In this presentation, we demonstrate that CDWs can be created via mechanical stress, which effectively avoids the potential problem of current leakage.

Here, an in-situ straining transmission electron microscopy technique was used to explore the structural evolution of ferroelectric domains introduced by mechanical stressing. Barium titanate micro-pillars were prepared using the focused ion beam technique. Mechanical loading was applied along a <100> direction. A high density of fine nanoscale domain walls formed when a pillar was compressed. Electron diffraction patterns of pillars with and without mechanical loading confirmed that all the newly created domain walls were CDWs. The original domain structure was restored with the full retraction of the external stress. The mechanism of the stress-induced evolution of domain wall structures will be discussed in detail. Our discovery is very important for the investigation of electromechanical properties of ferroelectrics.

ES21.07.30
Piezoelectric Acoustic Sensor Based on Two-Dimensional MoS$_2$ Hyoung Taek Kim, Ahrum Sohn, Jae Hwan Jung and Sang-Woo Kim; School of Advanced Material Science and Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Experimental studies on the physical properties of two-dimensional (2D) materials have grown exponentially since 2D materials offer unique advantages for use in such next-generation devices. Various semiconducting 2D materials have been studied, including transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS$_2$), molybdenum diselenide (MoSe$_2$) and tungsten diselenide (WSe$_2$), which are likely to bring breakthroughs in future electronic and optoelectronic devices. The physical properties of 2D MoS$_2$ nanosheets have been actively explored particularly as a result of their possible integration in both nano/microelectromechanical devices and energy harvesting devices. Monolayer MoS$_2$ has a direct band gap and high mobility and it has been used to successfully fabricate field-effect transistors so it has emerged as an interesting complement to graphene in various semiconductor applications. In addition it is expected that piezoelectric properties of 2D layered materials are very useful to realize high sensitive, high impact resistive, self-powered sensor. However, studies on the suspended model of 2D MoS$_2$ have been done mainly on studies on the measurement method or photosensitivity, and studies using the piezoelectric characteristics of suspended MoS$_2$ have not been actively done. Here we report a new way to use 2D MoS$_2$ for high sensitive 2D piezoelectric acoustic sensor. The acoustic sensor fabricated by using suspended structure of MoS$_2$ which generate piezoelectric output potential due to vibration transmitted by sound. We have achieved high sensitivity and high impact resistance by using single layer or several layers of MoS$_2$, and by using piezoelectric properties of MoS$_2$, we have produced an acoustic sensor that does not require standby power. This study demonstrates a new way of studying 2D MoS$_2$-research and acoustic sensors by developing a high-sensitivity and high-durability acoustic sensor using suspended MoS$_2$.

ES21.07.31
Direct Current Generator Based on Microdischarge via Accumulation of Triboelectric Charge in Atmospheric Condition Minki Kang, Hong Joon Yoon and Sang-Woo Kim; School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

A Triboelectric generator (TEG) is one of the most promising energy harvesters for powering electronics or sensors, conversing abundant kinetic energy to electrical energy. TEG generates displacement current according to triboelectric surface charge and electrostatic induction by periodic motion. Fundamentally, the surface charge density on triboelectric layer greatly affects to output performance of TEG and there have been numerous intensive studies to increase surface charge density. The surface charge density has been increased dramatically using advanced materials such as nanocomposite, ferroelectric materials or fluorinated materials. However, high surface charge density induces the microdischarge generation and upper configuration of available surface charge density in certain TEG mode becomes new challenge for next-generation high performance TEG. Here, we propose direct current generator based on microdischarge via accumulation of triboelectric charge in atmospheric condition. Microdischarge based direct current generator TEG (MD-TEG) employs in-plane configuration of each layer, electrode layer, rotor and segment layer. Also there is gap of sub-millimeter scale between electrode and rotor. These structural characteristics enable accumulation of huge amount of triboelectric charge in atmospheric condition and efficient charge-conveying those who are essential for high
output performance. Based on the novel working mechanism and structural characteristics of CSTEG, we found out that it can generate maximum output current of 12.2 mA/m² in RMS value under 1000 rpm.

**ES21.07.32**

**Multi-Functional Robust Reduced Graphene Oxide–Poly(vinylidene fluoride-trifluoroethylene) Flexible Nanocomposite Thin Film for Efficient Green Energy Harvesting**

Ritamay Bhunia and Ashish Garg; Indian Institute of Technology-Kanpur, Kanpur, India.

Nowadays, energy is an essential factor to sustain in our day-to-day life. The adverse effect of the mostly used energy sources fossil fuels are driving the researchers towards the alternative renewable energy research. Nanogenerators (NGs) have brought revolution in the energy harvesting research field. Modern civilization is using wireless smart nanodevices which are potentially used in sensing, monitoring of environmental state, industry, medical sciences, defense. Proliferation of using these electronic devices has raised a demand of fabrication of self-powered devices to replace battery. As ignited by the invention of piezoelectric nanogenerators (PE-NGs) in 2006[1], people are trying to harnessing electrical energy from various mechanical energies worldwide for self-powering devices at cost-effective ways. Different strategies were followed to boost up the output power level of the PE-NGs with different piezoelectric materials and various novel structures. In 2012, another more efficient and flexible, robust, low cost fabricated device named triboelectric nanogenerator (TE-NG) for harvesting energy was demonstrated by Z. L. Wang and his group.[2] So, till then these two devices have got more attention due to suitable power density, durability, flexibility, cheap device fabrication, wide material choice and outstanding adaptability to green energy sources.[3] Considering this scenario, there is urgent need for an acceptable material which can serve high output power densities with reliable time duration and can mold on any curve surface at low-cost.

Through this present work, a multi-functional eco-friendly flexible material has been presented which can be used as efficient energy harvester from ambient mechanical energies as well as ferroelectric memory device (Fe-RAM) material. We fabricated both flexible PE-NG and TE-NG of area 4x4 cm² made of reduced graphene oxide–Poly(vinylidene fluoride-trifluoroethylene) nanocomposite thin films (6-7 mm) processed through low-cost sol-gel way. Self-alignment of reduced graphene oxide (rGO) in the composite depends on different phenomena like p-p interaction between carbonyl, carboxyl functional groups of basal planes of rGO and P(VDF-TrFE), van der waals force between the nearest rGO sheets, excluded volume interaction, steric hindrance.[4] These interactions broke the centro-symmetry of rGO and piezoelectric property was induced in rGO, which further enhanced the ferroelectric, piezoelectric properties in polymer nanocomposite.[5] Due to the presence of negative functional groups attached with planes of rGO nano-flakes, it also improved the composite as a negative triboelectric material and the TE-NG performance. This was further confirmed measuring surface potential after inclusion of rGO in P(VDF-TrFE) through KPFM technique. Thus, this composite can serve as an efficient multi-functional material for energy harvesting and memory application. Piezo Force Microscopy (PFM) showed formation of more ferroelectric domains in case of composite than pristine P(VDF-TrFE). Remnant polarization (P_r) and dielectric constant increased 13.3 % and 150% from 7.18 mC/cm² and 14 of pristine polymer, respectively due to the space charge formation between interface of insulating polymer and slightly conducting rGO sheets. The highest piezoelectric co-efficient (d_33) was observed -80.19 pC/N in case of an optimum rGO concentration in polymer matrix, where the value for pristine polymer was -41.37 pC/N. The average PE-NG output voltage (V_max) made of polymer composite was measured 62 V (maximum 75 V) attaching the device on a wall of small rotary pump for 30 minutes continuously, while virgin polymer films showed 1.1 V. An average 190 V V_max was recorded from TE-NG of highest rGO content polymer nanocomposite. The maximum output power densities through 1 MW load resistance of PE-NG and PE-NG devices were 222 and 32 mW/cm². We were able to glow 20 LEDs in parallel directly by just 3 fingers tapping using TE-NG.

**ES21.07.33**

**Flexible PVDF Nanocomposite Films for Enhanced Piezoelectric Effect**

Neeraj Khare and Huidrom Hemojit Singh; Indian Institute of Technology Delhi, Hauz Khas, India.

The number of electronic devices used in our daily life has been increasing tremendously since the last decades. Several devices require only few milli-watt power. Piezoelectric nanogenerators based on the flexible piezoelectric polymers mainly Polyvinylidene fluoride (PVDF) is a path-breaking device that can power these small-scale electronic devices directly [1-2]. Although the intrinsic piezoelectric property of PVDF is low, many methods have been employed to enhance the piezoelectric property like thermal treatment, mechanical stretching and electrical poling [3]. In the present work, we will compare the performance of piezoelectric nanogenerator fabricated using various PVDF nanocomposite films. We have achieved enhanced piezoelectric property of PVDF just by adding nanostructures such as ZnO, NaNbO_3, BaTiO_3 without any further heat, electrical or mechanical treatment. XRD, polarization-electric field (P-E) measurement, Fourier transform infrared spectroscopy (FTIR) measurements have been performed, and the reason behind this enhancement in the piezoelectric property has been analyzed and discussed. We have compared the enhancement by adding a different amount of nanofillers of different shapes, and this gives a brief idea of choosing the appropriate nanofillers for enhancing the piezoelectric property of PVDF. Comparison of the performance of these nanogenerators fabricated from PVDF nanocomposites will be presented.

**References**


**ES21.07.34**

**Deep-Trap Dominated Sustainable Mechanoluminescence from Layered Perovskite SrSnO_3:Sm^3+ Dong Tu** and Chao-Nan Xu; 1Wuhan University, Wuhan, China; 2National Institute of Advanced Industrial Science and Technology, Tsu, Japan.

Mechanoluminescence (ML) from purely inorganic materials is basically triggered by a pre-UV-irradiation process, which largely limits its practical applications. Here, by designing a pinning-trap structure, a novel sustainable ML is developed from Ruddlesden–Popper perovskite SrSnO_3:Sm^3+ even without the pre-UV-irradiation process. This ML of SrSnO_3:Sm^3+ could keep stable and maintain a certain intensity even extending the wait time to 50 h. ML mechanism is also investigated by analysis of trap structure through the thermoluminescence method. A thermoluminescence peak at 420 K showed no attenuation after 50 h waiting time, which could be ascribed to a high-density pinning trap, result in the increase in the ML intensity and ML intensity maintenance ratio.

**ES21.07.35**

**Triboelectric Nanogenerator Networks Integrated with Power Management Module for Water Wave Energy Harvesting**

Tao Jiang, Xi Liang, Guoxu Liu; Chi Zhang; Zhong Lin Wang; Georgia Institute of Technology, Atlanta, Georgia, United States.

Ocean waves are one of the most promising renewable energy sources for large-scale applications. Recently, triboelectric nanogenerator (TENG) network has been demonstrated to effectively harvest water wave energy possibly toward large-scale blue energy. However, the absence of effective power management severely restricts the practicability of TENGs. In this work, a hexagonal TENG network consisting of spherical TENG units based on spring-assisted multilayered structure, integrated with a power management module (PMM), was constructed for harvesting water wave energy. The output performance of the TENG network was determined by wind wave frequencies and amplitudes, as well as the wave type. Moreover, with the implemented PMM, the TENG network could output a steady and continuous direct current (DC) voltage on the load resistance, and the stored energy was dramatically improved by up to 96 times for charging a capacitor. The TENG network integrated with the PMM was also applied to effectively power a digital thermometer and a wireless transmitter. The thermometer can constantly measure the water temperature with the water wave motions, and the transmitter can send signals for alarming once every 10 s. This study extends the application of the power management module in the water wave energy harvesting.

**ES21.07.36**

**Piezotronic Magnetoelectric Sensors for Biomedical Diagnostics**

Mona M. Mintken, Sören Kaps, Yogendra K. Mishra, Jürgen Carstensen and Rainer Adelung; Kiel University, Kiel, Germany.

Advanced medical diagnostics tools like magnetoencephalography (MEG) and magnetocardiography (MCG) require sensors that can detect low frequency magnetic fields of very...
small amplitudes in the nano- to sub-picotesla range. Superconducting quantum interference device (SQUID) sensors, which are state of the art in these applications, have several drawbacks including the need of cooling, operation in sheltered chambers and high cost. Magnetoelastic (ME) sensors are currently developed as a promising alternative. The working principle of ME composite sensors relies on a magnetostrictive layer, which translates the change in magnetic field into mechanical deformation. It is mechanically coupled to a piezoelectric layer to convert the mechanical strain into electric voltage.

The piezotronic effect can be employed for realizing the ME sensor signal to improve the limit of detection (LoD), which is the smallest measurable magnetic field normalized to an equivalent noise bandwidth of 1 Hz. One of the two electrodes attached to the piezoelectric component of the sensor is chosen to be a material which forms a Schottky type contact with the piezoelectric material, while the second electrode forms an Ohmic contact. The electric field generated in the piezoelectric material when it is deformed changes the charge carrier transport characteristics across the Schottky contact drastically. This effect replaces an external amplifier for the sensor signal (in this case a piezotronic current), leading to lower noise and reduced power consumption compared to conventional voltage read-out.

Two kinds of ME sensors have been investigated here: one is a cleanroom-fabricated MEMS cantilever type sensor that consists of magnetostrictive FeCoSiB and piezoelectric AlN. The other sensor type consists of a single crystalline ZnO needle mounted on a piece of magnetostrictive foil. The variation of parameters such as doping, defects and stress in the material and geometry, contact configuration, electric and magnetic bias fields and read-out process of the sensor setup leads to a deeper understanding of the piezotronic effect and is expected to increase the performance of various ME sensor types.

In the present work, we have analyzed the time signal of the ME sensors to further understand the noise sources and reduce the noise floor of the sensor system by customized digital signal processing.

ES21.07.37

High Sensitive Self-Powered Triboelectric Auditory Sensor for Social Robotics and Hearing Aid Hengyu Guo1,2,3,1, Xiaojie Pu2, Chenguo Hu1 and Zhong Lin Wang1,2,3; Georgia Institute of Technology, Atlanta, Georgia, United States; ‘Chongqing University, Chongqing, China; ‘Beijing Institute of Nanoenergy & Nanosystems, Beijing, China.

The auditory system is the most efficient and straightforward communication strategy for connecting the human beings and robots in the upcoming artificial intelligent (AI) era. Here, we design a self-powered triboelectric auditory sensor (TAS) for constructing a new electronic auditory system and further applying as the architecture of external hearing aid in intelligent robotic applications. Based on the unique working mechanism of newly developed triboelectric nanogenerator (TENG) technology, the TAS shows ultra-high sensitivity (110 mV/µB). TAS with the broadband response from 100 to 5000 Hz is achieved by designing the annular or sectorial inner-boundary architecture with systematical optimization. Incorporating with intelligent robotic devices, TAS demonstrates a capability of high-quality music recording and accurate voice recognition for realizing intelligent human-robot interaction. Furthermore, the fascinating feature of TAS with tunable resonant frequency can be achieved by adjusting the geometric design of inner-boundary architecture, which can be used to amplify a specific sound wave naturally. Based on this unique property, we propose a new type of hearing aid with TENG technic, which can simplify the signal processing circuit and reduce the power consuming. This work expresses significant advantages of using TENG technology to build a new generation of auditory systems for meeting the challenges in social robotics.

ES21.07.38

Self-Powered Multifunctional Motion Sensor Enabled by Magnetic Regulated Triboelectric Nanogenerator Zhiyi Wu, Wenbo Ding, Yejing Dai and Zhong Lin Wang; Georgia Institute of Technology, Atlanta, Georgia, United States.

With the fast development of Internet of Things, the requirements of system miniaturization and integration have accelerated research on multifunctional sensors. Based on the triboelectric nanogenerator, a self-powered multifunctional motion sensor (MFMS) is proposed in this work, which is capable of detecting the motion parameters, including direction, speed, and acceleration of linear and rotary motions simultaneously. The MFMS consists of a triboelectric nanogenerator (TENG) module, a magnetic regulation module, and an acrylic shell. The TENG module is formed by placing a free-standing magnetic disk (MD) on a polytetrafluoroethylene (PTFE) plate with six copper electrodes. The movement of the MD causes the MD to slide on the PTFE plate and hence excites the electrodes to produce voltage output. The carefully designed six copper electrodes (an inner circle electrode, an outer circle electrode, and four arc electrodes between them) can distinguish eight directions of movement with the acceleration and determine the rotational speed and direction as well. Besides, the magnetic regulation module is applied here by fixing a magnetic cylinder (MC) in the shell, right under the center of the PTFE plate. Due to the magnetic attraction applied by the MC, the MD will automatically return to the center to prepare for the next round of detection, which makes the proposed sensor more robust and more applicable in practice.

ES21.07.39

Ultrasensitive and Highly Selective Self-Powered Room Temperature NO2 Detection Enabled by Triboelectric Nanogenerator Yuanjie Su, Guangzhong Xie, Huiling Tai, Xiaosong Du and Yadong Jiang; University of Electronic Science and Technology of China, Chengdu, China.

With increasing vehicle ownership and environment pollution, the release of nitrogen dioxide (NO2) and its derivatives have considerably posed a threat to human health and public security. By far, various approaches have been applied to develop a reliable, accurate and sensitive approach for NO2 detection, including field effect transistor (FET), surface acoustic wave (SAW), bulk acoustic wave (BAW), resistance, quartz crystal microbalance (QCM). However, all of these sensing techniques are demanded for a power supply which undoubtedly renders incredible high cost and complexity. In addition, considering the tremendous number and wide distribution of gas sensor networks, it is unrealistic to continuously sustain the availability of the external power source and replace the battery for each device especially in wilderness and extreme environment. Therefore, a simple, robust and low-cost gas sensor operated by scavenging ambient energy is desperately desired.

In this work, a triboelectric nanogenerator (TENG) driven self-powered gas sensor has been developed for room temperature nitrogen dioxide (NO2) detection under UV illumination (365 nm). Powered by TENG, the concentration of NO2 can be spontaneously detected via chemoresistive gas sensor based on Zinc Oxide-Reduced graphene oxide (ZnO-RGO) hybrid films, where the voltage drop across the interdigital electrodes (IDEs) has a proportional relationship with NO2 concentration. The self-powered triboelectric gas sensor (TGS) comprised by ZnO-RGO composite films exhibit superior response (~16.8) and sensitivity as well as selectivity that for pure ZnO film. With respect to selectivity, the response of ZnO-RGO composite film based TGS to NO2 was at least 49-fold higher than those for other gases. Furthermore, through a signal processing circuit, a self-powered NO2 gas alert system was developed for real-time monitoring the ambient NO2 concentration. This work not only promotes the applicability of TENGs as self-powered sensors but also pushes forwards the active sensing network node for environmental monitoring by harvesting ambient energy.

References: (*indicate corresponding author)

ES21.07.40

Piezotronic Effect In 1D Solid of Elemental Tellurium Nanobelt for Smart Adaptive Electronics Shengjie Gao1,2, Yixiu Wang1,2 and Wenzhuo Wu1,2; Purdue University, West Lafayette, Indiana, United States; 1Flex Laboratory, West Lafayette, Indiana, United States.

Emerging technologies in wearable systems demand that functional devices can adaptively interact with the human body, where mechanical stimuli are ubiquitous and abundant. However, the electrical manipulation of charge carriers underpins the operations of state-of-the-art devices, and the effective control of interfacial energetics for charge carriers by the dynamic mechanical stimuli is still a relatively unexplored degree of freedom for semiconductor nanodevices. Piezotronic effect in nanostructured piezoelectric semiconductors offers exciting opportunities in addressing the above challenges. Here we report the first experimental exploration of piezotronic effect in 1D solid of p-type tellurium nanobelt and systematically investigate the strain-gated charge carriers transport properties. The strain-induced polarization charges at the [1010] surfaces of Te nanobelt can modulate the electronic transport through the interfacial effect on the Schottky contacts and the volumetric effect on the conducting channel. The competing phenomenon between interfacial
and volumetric effects has been studied for the first time in piezotronics. Our research allows the access to a broad range of characterization and application of Te nanomaterials for piezotronics and could guide the future study of piezotronic effect in other materials. This progress in piezotronics, together with emerging methods for deterministic production and assembly of nanomaterials, leads to compelling opportunities for research from basic studies of piezoelectricity and semiconductor properties in functional nanomaterials to the development of “smarter” electronics and optoelectronics.

ES21.07.41
Engineered and Laser Processed Chitosan Biopolymers for Sustainable and Biodegradable Triboelectric Power Generation Ruoxing Wang and Wenzhuo Wu; Purdue University, West Lafayette, Indiana, United States.

Triboelectric nanogenerator (TENG) is regarded as a promising technology to replace traditional power source by converting mechanical energy to electricity. However, most TENGs are made from materials that are not biocompatible, which limits their applications in biomedical and implanted applications. Here we report for the first time the development of low-cost, biodegradable and flexible triboelectric nanogenerators based on chitosan, which is one of the most abundant biopolymers on earth and can be derived from the shells of shrimp or other sea crustaceans. Tunable electrical outputs were achieved by either mixing the chitosan with other natural materials such as starch and lignin or through laser processing. The chitosan-based TENGs present efficient energy conversion performance and the optimized chitosan-based power source can be used for water purification by taking advantage of the electrostatic attraction effect and chelation with contaminants in the water. The new class of TENGs derived from natural materials may pave the way towards the economically viable production of flexible TENGs for self-powered nanosystems in biomedical and environmental applications.

ES21.07.42
Solution-Synthesized Chiral Piezoelectric Selenium Nanowires for Wearable Self-Powered Human-Integrated Monitoring Min Wu, Yixiu Wang, Shengjie Gao, Ruoxing Wang and Wenzhuo Wu; Purdue University, West Lafayette, Indiana, United States.

Smart sensing devices with high stretchability and self-powered characteristics are essential in future generation wearable human-integrated applications. Here we report for the first time scalable synthesis and integration of selenium (Se) nanowires into wearable piezoelectric devices, and explore the feasibility of such devices for self-powered sensing applications, e.g., physiological monitoring. The ultrathin device can be conformably worn onto the human body, effectively converting the imperceptible time-variant mechanical vibration from human body into distinguishable electrical signals, e.g., gesture, vocal movement, and radial artery pulse, through straining the piezoelectric Se nanowires. Our results suggest the potential of solution-synthesized Se nanowire a new class of piezoelectric nanomaterial for self-powered biomedical devices, and opens doors to new technologies in energy, electronics, and sensor applications.

ES21.07.43
Nanocomposites Electret with Unique Surface Potential Self-Recovery Characteristics for Harvesting Mechanical Energy in Extreme Environment Huayang Li and Guang Zhu; University of Nottingham Ningbo China, Ningbo, China.

Developing the electrets that can withstand harsh environments are playing an important role in harvesting mechanical energy in extreme cases. Here we report a new nanocomposites electret material that exhibit efficient self-recovery of the surface potential after water dipping. The surface charge density can reach 0.5 mC/m² and the surface potential can recover to 90% of its initial value in 60 mins after fishing out. The electret nanogenerator based on this electret can effectivly harvest mechanical energy and the high output power is 54 mW. Moreover, the electric output can self-recover by 90% in 10 mins without any other friction cycles. With a power management circuit, the electret-nanogenerator-based power-supplying system can used to power a wireless emitter. Given the self-recovery property of this new electret and the electret nanogenerator, this study broadens new perspectives for promoting the wearable devices in extreme environments.

ES21.07.44
Mapping Pressure with Flexible and High-Resolution p-GaN/n-ZnO Nanowires Arrays by Piezo-Phototronic Effect Yiyou Peng and Caofeng Pan; Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China.

Simulating human tactile sensing through high-resolution electronics is a significant and challenging topic in the field of artificial intelligence. Compared with the senses of sight, smell, hearing, and taste, touch remains stubbornly difficult to mimic, which needs the development of large-sized pressure sensor arrays possessing high-spatial resolution, high-sensitivity, fast-response [1, 2]. The rapidly developing flexible LED arrays can be employed as a strain sensor to indicate the pressure distribution through different light emission intensities [3, 4]. GaN, as an ideal semiconductor material for short-wavelength optoelectronics, has long been a grand challenge to be used for flexible light-emitting devices due to the rigid epitaxial substrate.

In our work, we fabricated a flexible and high-resolution p-GaN/n-ZnO nanowires heterostructure light-emitting diode (LED) arrays, the light emission of which is enhanced by piezo-phototronic effect. Specifically speaking, a flexible p-GaN film/n-ZnO nanowires light-emitting diode (LED)-based pressure sensor array, with the merits of flexibility, high resolution, fast response, good transparency, stability, and lightweight, is fabricated through laser lift-off (LLO) process and used to acquire the two-dimensional pressure distribution mapping by reading the illumination intensities from all LED pixels parrelally. The intensity of each pixel composed by a GaN/ZnO nanowire heterostructure LED can be enhanced by the local compressive strain based on piezo-phototonic effect. A high spatial resolution of 2.6 um, a fast response time of 180 ms and a relatively wide measurement region were obtained, and the sensor array can still function well after 4000 bending circles.

The approach is scientifically novel to combine the advantages of high resolution and fast response in regard to rigid GaN substrate LED and flexibility of organic LED, which may be more easily applied in highly intelligent and flourishing human-machine interfaces and make an important step in flexible photonic integration technology, with potential application prospects in smart skin, touch panel technology, biomedicine science, and optical MEMS.

ES21.07.45
Strain Modulation Band Alignment of Monolayer MoS2/ZnO Nanorod Mixed-Dimensional Heterostructure Arrays for Efficient Charge Transfer Baishan Liu1,2, Qingliang Liao1, Zhao Kang1 and Yue Zhang1,2; 1State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China; 2Beijing municipal key Laboratory for advanced Energy Materials and Technologies, University of Science and Technology Beijing, Beijing, China.

The isolation of extraordinary two-dimensional (2D) semiconductors has inspired worldwide efforts to form van der Waals heterostructures for promoting electronic and optoelectronic applications. Due to the ultra-strength of 2D materials, strain engineering offers a new strategy for tailoring properties of heterostructures. However, this approach requires a stable method to apply strain and an understanding of strain effects on the band alignment of heterostructures. Here, we construct periodic-strained monolayer MoS2/ZnO heterostructure via nanoindentation from tailored ZnO nanopatterns. Sufficient comparison of photoluminescence (PL) measurements clearly verifies that strain can efficiently tune the band gap of MoS2 and enhance charge transfer efficiency from MoS2 to ZnO. Eventually, we demonstrate that enhanced charge transfer efficiency is attributed to strain modulation on the band alignment of MoS2/ZnO. These findings highlight strain engineering for optimizing the band alignment of heterostructure and potentially pave the way to design integrated optoelectronics or photovoltaics with novel functions.

ES21.07.46
Networks of High Performance Triboelectric Nanogenerators Based on Liquid-Solid Interface Contact Electrification for Harvesting Low-Frequency Blue Energy Juan Tai and Caofeng Pan; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

Energy crisis has become one of world's most serious challenges, as the rapid growth of the total energy consumption. The renewable energies have been intensively explored and converted into electricity to ensure the sustainable development. The inexhaustible blue energy from the ocean is independent of season, circadian rhythm and weather. At the same time, triboelectric nanogenerators (TENGs) are considered as one of the most promising approaches for harvesting blue energy. Previously, most of the blue-energy-harvesting TENGs are based on the friction between solids, but the contact / friction area is only a tiny portion of the total surface due to the roughness of the surface and the inefficient contact condition.
In this work, a network of liquid-solid-contact triboelectric nanogenerator (LS TENG) is fabricated to efficiently harvest the huge quantities of blue energy from ocean. Due to the sufficient contact condition of the liquid solid interface, the energy output per cycle of LS TENG is about 48.7 times bigger than that of the solid-solid-contact triboelectric nanogenerator (SS TENG) with same area. The buoy LS TENG can generate several sequential damping signals just by one pulse of triggering, demonstrating the maximum utilization of the vibration energy. This characteristic merit renders it available for the buoy LS TENG to collect the low-frequency current efficiently. The output current, transferred charge and the output voltage of the network of 18 LS TENGs are 290 µA, 16725 nC and 300 V.

Additionally, the buoy LS TENGs could harvest large quantities of energy, including surface wave energy and submarine current energy, to power portable electric devices or navigation systems. In this work, the electricity generated from the LS TENGs is stored in the capacitor to drive a wireless SOS radio frequency (RF) transmitter for ocean emergencies. This work provides a more efficient method of capturing the blue energy and expands its applications.

Reference:
with smaller width and the mode positions can be modulated dynamically. The relationship between the corresponding applied strain and the tunable refractive index is analyzed in depth and discussed systematically. This method will open new horizons in understanding and utilizing the piezoelectric properties of lead halide perovskites.

ES21.07.50
An Ultralight, Self-Powered and Self-Adaptive Motion Sensor for Perceptual Layer Application in Internet of Things Xuan Zhao, Xiaochen Xun, Fangfang Gao, Qingliang Liao and Yue Zhang; University of Science and Technology, Beijing, China.

In the Internet of things (IoT), motion sensor in the perceptual layer is at the forefront of the information collection, which plays a crucial role in the IoT. However, with a large number of commercial applications, several problems of motion sensor limit the development of IoT such as poor portability, poor environmental adaptability, and high energy consumption, etc. In this work, an ultralight, self-powered and self-adaptive motion sensor (UMS) is reported. Total mass of the UMS is less than 20 mg. Zero energy consumption of the UMS is achieved by the coupling of triboelectricity and electrostatic induction. Moreover, the UMS shows satisfactory self-adaptive performance of both temperature and humidity, less-sensitive to temperature in surroundings, from 5 degrees Celsius to 60 degrees Celsius, and ambient humidity under 90% RH. Furthermore, sensing signals triggered by different motion behaviors, such as grasping, walking, stooping and so on, can be distinguished by the processor clearly, which can be applied to motion recognition and machine control. This work presents a novel UMS with characteristics of portability, energy conservation and environmental friendliness. The UMS shows broad prospect in perceptual layer application in IoT.

ES21.07.51
Ultrafast, Sunlight-Triggerable Transient Energy Harvester and Sensors Based on Triboelectric Nanogenerator Using Acid-Sensitive Poly(phthalaldehyde) Changsheng Wu, Jiun Jiang, Hengyu Guo, Paul Kohl and Zhong Lin Wang; Georgia Institute of Technology, Atlanta, Georgia, United States.

Transient electronics that can degrade under certain circumstances have great potential in biomedical and military applications. Depending on constituting materials, the transient purpose can be achieved either through material dissolution or depolymerization. Material demploymization can be achieved through variable stimuli, such as humidity, temperature, chemical, or light. Meanwhile, triboelectric nanogenerator (TENG), an emerging mechanical energy harvesting technology that has great flexibility in material choices, is promising in offering transient power sources. Pioneering efforts have been made on biodegradable TENGs using biodegradable polymers such as polyglycolic acid and poly(lactic acid) for implantable power sources. However, these TENGs only offer solution-based degradation and have limited application in non-biological scenarios. In this work, we developed the first TENG whose degradation can be triggered simply by sunlight and completed in a short time span. Its main substrate was made of the acid-sensitive poly[(phthalaldehyde) (PPHA), a photo-acid generator (PAG) called tetraakis(hexafluoro-2,5-dioxo-1,4-pentanone)diborane, and a sensitizer called anthracene. The sensitizer was used to absorb and transfer the energy of UVA light (365 nm) to PAG via photo-induced electron transfer, while the latter generates protons to trigger the depolymerization of PPHA. The triboelectric properties of this PPHA-based material were studied, which suggested that it locates at the more positive side in the triboelectric series than nylon. Transient TENG-based biomechanical energy harvester and tactile sensors were successfully demonstrated by embedding silver nanowires into the PPHA-based films. Therefore, this work not only broadens the applicability of TENG as transient power sources, but also expands the use of functional polymers towards advanced energy and sensing applications.

ES21.07.52
Piezoelectric Gated Interfacial Charge Modulation in WSe2-ZnO Mixed-Dimensional Van Der Waals Heterostructures for Ultrasensitive Flexible Photodetectors Jun Li, Zheng Zhang, Qingliang Liao, Zhiuo Kang and Yue Zhang; Beijing Municipal Key Laboratory for Advanced Energy Materials and Technologies, University of Science and Technology, Beijing, China; School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China; State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China.

Van der Waals (vdWs) heterostructures based on atomically thin 2D materials have led to a new age in next-generation flexible optoelectronics, due to their excellent bending strength, absence of bond fracture and atomic reconstruction under strain.[1] Furthermore, gate-tunability of van der Waals (vdWs) material is crucial for modulating performance of vdWs optoelectronics. [2] However, the conventional electrostatic gating has met severe challenges in flexible optoelectronics owing to in-plane cracking and slippage of gate electrode under strain. So far, most of the reported flexible photodetector based on 2D materials suffer from low sensing performance. Here, we propose a distinctive strain-gating method to achieve high performance flexible photodetector by combining the strong light-material interaction in 2D WS2 and excellent piezoelectric property of 1D ZnO. The photodetector shows a good photovoltaic response under a defined white light illumination intensity of 0.667 mW/cm2 by a halogen lamp. By modulating with strain-induced piezopolarization charges in ZnO, short-circuit current of photodetector was enhanced by 2 times under a tensile strain of 0.87%. Under photoconductive mode, the photocurrent was improved to 320 pA, and responsivity up to 0.394 A/W. Enhancement of the sensing performance is attributed to local energy-band tilting at the piezo-modulated WSe2-ZnO interface. In particular, these piezopolarization charges lead to increase of built-in electric field in heterojunction and accelerate the separation of photo-excited electron-hole pairs, which ultimately promotes the photoresponsivity of the device. Our work provides a new strategy to achieve interaction between vdWs interface and strain stimuli, which may broaden applications of functional vdWs heterostructure for next-generation visible detecting or imaging.

References:

ES21.07.53
Super-Stretchable and Mechanically-Durable Triboelectric Nanogenerators for Deformable and Wearable Energy Sources and Self-Powered Electronic Skins Ying-Chih Lai1,2,3, Changsheng Wu1,2,3, Zheng Zhang4, Qingliang Liao2 and Yue Zhang1; 1Department of Materials Science and Engineering, National Chung Hsing University, Taichung City, Taiwan; 2Research Center for Sustainable Energy and Nanotechnology, National Chung Hsing University, Taichung City, Taiwan; 3Innovation and Development Center of Sustainable Agriculture, National Chung Hsing University, Taichung City, Taiwan.

Wearable and stretchable electronic devices have attracted great interest because they cannot only extend the application scope of electronic systems but also provide compliant user experience. Driving those devices inevitably need power sources. However, conventional batteries suffer from not only heavy weight and bulky volume but also limited capacity and lifetime, handicapping the progress and practical uses of those emerging devices. In this present, super-stretchable and mechanically-durable triboelectric nanogenerators (SD-TENGs) will be demonstrated by using composed of intrinsic stretchable components. The newly-designed SD-TENGs can generate electricity from contact capacity and lifetime, handicapping the progress and practical uses of those emerging devices. In this work, we developed the first TENG whose degradation can be triggered simply by sunlight and completed in a short time span. Its main substrate was made of the acid-sensitive poly(phthalaldehyde) (PPHA). The sensitizer was used to absorb and transfer the energy of UVA light (365 nm) to PAG via photo-induced electron transfer, while the latter generates protons to trigger the depolymerization of PPHA. The triboelectric properties of this PPHA-based material were studied, which suggested that it locates at the more positive side in the triboelectric series than nylon. Transient TENG-based biomechanical energy harvester and tactile sensors were successfully demonstrated by embedding silver nanowires into the PPHA-based films. Therefore, this work not only broadens the applicability of TENG as transient power sources, but also expands the use of functional polymers towards advanced energy and sensing applications.

[Ref]

ES21.07.54
Harsh-Environmental-Resistant Triboelectric Nanogenerator Baodong Chen; Beijing Institute of NANOenergy and Nanosystems, Beijing, China.

We report a device suitable for harsh environmental applications based on the wear-resistant triboelectric material. The working modes of the harsh-environmental TENG (heTENG) was composed of freestanding mode and single electrode mode that enables both harvesting sliding/vibration energy and self-powered vibrational sensing. For the first
time, the TENG possessing wear resistance, withstanding high temperature and high hardness is achieved by employing micro-nano composite for triboelectric materials. It is demonstrated to be directly used as a key supporting part, such as automobile's brake pads. In addition, it is found that the heTENG outputs 221 V, 27.9 μA/cm² and 33.4 μC/cm². Furthermore, since the heTENG is vibration-sensitive, the automobile's self-powered smart braking (SP-SB) system and sensor network are developed successfully which can automatically provide exact early-warning signal, such as a reminding of the brake's replacement, vehicle overweight, and tire pressure variation. Our work shows a new strategy to enhanced the performance of triboelectric materials, making it applicable to harsh environment, and also provides new opportunities for sliding/vibration energy harvesting and self-powered vibrational sensing, as well as potential applications in autonomous vehicles and industrial brakes.

**ES21.07.55**

**Silicon-Based Spintronics—Experimental and Theoretical Validation of Spin Manipulation in Silicon**  
Paul Lou, Sun Ken, Pengfei Wang, and Dongfeng Diao; 1 Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, Xi'an Jiaotong University, Xi'an, China; 1 Institute of Nanosurface Science and Engineering (INSE), Guangdong Provincial Key Laboratory of Micro/Nano Optomechantronics Engineering, Shenzhen University, Shenzhen, China.

As a revolutionary energy harvesting technology, triboelectric nanogenerator (TENG) has attracted the worldwide attention for its distinguished properties and wide application as self-powered sensors since it was invented. A common challenge for sliding-mode TENG was surface friction induced materials abrasion and electrical output performance degradation in mechanical energy harvesting under long-term continuous work. Clarify the effect of friction force on the electrical output performance of sliding-mode TENG not only can improve its output performance but also provide a guideline in the structure design of TENG. In this work, a series of experiments were designed and conducted to reveal the effects of the friction force on the electrical output performance of three kinds of sliding-mode TENG, namely, metal-dielectric, semiconductor-dielectric and dielectric-dielectric. The results showed that the short-circuit output current and the open-circuit voltage of the metal-dielectric sliding-mode TENG increased with the increase of sliding friction force. More importantly, we found that with an excitation induced by friction force the short-circuit output current of the metal-dielectric sliding-mode TENG showed an inverse tendency compared with the short-circuit output current under a changeless friction force. In addition, it was found that a wave friction force has great benefit in enhancing the electrical output performance of metal-dielectric sliding-mode TENG. These findings not only reveal the effect of friction force on the electrical output performance of sliding-mode TENG but also provide a guideline for designing and optimizing the structure of TENG to efficiently harvesting mechanical energy.

**ES21.07.57**

**Friction Force Effect on the Electrical Output Performance of Sliding-Mode Triboelectric Nanogenerator** Weiqiang Zhang, Kun Sun, Pengfei Wang, and Dongfeng Diao; 1 Key Laboratory of Education Ministry for Modern Design and Rotor-Bearing System, Xi'an Jiaotong University, Xi'an, China; 2 Institute of Nanosurface Science and Engineering (INSE), Guangdong Provincial Key Laboratory of Micro/Nano Optomechantronics Engineering, Shenzhen University, Shenzhen, China.

High-power devices, such as ultrasonic motors, underwater acoustic transducers and piezoelectric transformers, require piezoelectric ceramics with low dielectric loss tan δ, high mechanical quality factor Q_m (low mechanical loss), and simultaneously large piezoelectric constant d33 and electromechanical coupling factor k_p [1]. Many ternary and quaternary piezoelectric ceramics, such as Pb(Mg_{1/3}Nb_{2/3})O_3-Pb(Zr,Ti)O_3, Pb(M_{1/3}Nb_{2/3})O_3-Pb(Zn_{1/3}Nb_{2/3})O_3-Pb(Zr,Ti)O_3, etc. [2, 3] have been synthesized and modified by MnO, CoO, etc. to satisfy these requirements. However, it is still difficult to improve piezoelectric properties and reduce dielectric loss simultaneously. Herein we report our research work on the FeO_3 doped Pb(M_{1/3}Nb_{2/3})O_3-Pb(Zn_{1/3}Nb_{2/3})O_3-Pb(Zr,Ti)O_3 (PMnS-PZN-PZT) high-power piezoelectric ceramics. These ceramics possess a single-phase perovskite structure, and the addition of FeO_3 helps to acquire a dense morphology. FeO_3 doping also tailors the phase structure of the PMnS-PZN-PZT ceramics. Ceramics with FeO_3 content of 0.45 wt% exhibit a relatively large piezoelectric responses and extremely low losses, showing that the ceramics is suitable for the high-power applications. The electric field dependence of dielectric and piezoelectric properties in subswitching field range, and the effect of temperature on the nonlinearity of dielectric property are also investigated. The results show that the dielectric and piezoelectric constants gradually increase with the increase of electric field level. Rayleigh analysis reveals the contribution from lossless reversible domain wall motion to the high-field nonlinear dielectric and piezoelectric properties [4]. This behavior is associated with the orderly distribution of defect pinning centers, and is thought to be responsible for the low losses of the ceramics. At elevated temperatures, the mobility of the oxygen vacancies increases, so that the distributions of the defect pinning centers are gradually randomized, which consequently lead to the enhancement of high-field nonlinearity.

**References:**

**ES21.07.58**

**Piezoelectricity and Ferroelectricity in 2D Layered Materials for Electronic Devices** Xi Yuan, Hung-Liu Chan and Jianhua Hao; The Hong Kong Polytechnic University, Hong Kong, China.

Recently, piezoelectricity in 2D van der Waals (vdW) materials has attracted great interest owing to promising unique applications in nanoscale electromechanical systems, ultrasensitive sensors, high-precision actuators, piezotronics and piezo-piezotronics. Monolayer transition metal dichalcogenide MoS_2 with intrinsic in-plane piezoelectricity has been extensively addressed in recent years, which has great potential applications. However, the vertical piezoelectric response of MoS_2 is theoretically absent due to the inversion symmetry. Here, we report out-of-plane piezoelectricity and ferroelectricity in 2D layered material InSbSe_2. Specially, the piezoelectricity based on the InSbSe_2 is not limited by edge effect and layer-dependence. Moreover, the out-of-plane ferroelectricity in InSbSe_2 is also investigated by piezoresponse force microscope, which can retain the ferroelectric behaviour down to 6 nm. This work opens the door to explore ferroelectricity and piezoelectricity to the family of 2D layered materials which will create novel functionalities of both materials and atomic-scale electronic devices. The work was supported by the grant from Research Grants Council of Hong Kong (GRF No. PolyU 153033/17P).
Electrochemical techniques have been extensively applied to treat heavy metal pollution in our daily life. Considering the energy crisis in modern times, a self-sufficient power source that coupled with chemical processes for maximizing recycling efficiency of heavy metal ions using the least electricity, is a promising alternative for the simultaneous energy saving and environmental governance. Here we investigated the effects of constant current and impulse current on hexavalent chromium (Cr(VI)) removal. Compared with constant current, impulse current with higher frequency (10 Hz) can enhance the removal efficiency of Cr(VI) under the equal electric charges. Meanwhile, the removing efficiency Cr(VI) can be further improved by optimizing the on-off ratio of pulses. Based on the analysis, a pulsed direct-current output based on triboelectric nanogenerator (TENG) is obtained through designing pulse current waveforms. With only the electrical energy extracted from mechanical motions by the TENG, heavy metal pollutant such as Cr(VI) can be sufficiently and continuously removed.

8:15 AM *ES21.08.02
Fiber-Based Hybrid Energy Conversion Systems Bao Yang, Wei Zeng, Song Chen, Jian Song, ShiRui Liu, Shaping Lin, Lisha Zhang and Xiaoming Tao; Institute of Textiles & Clothing, The Hong Kong Polytechnic University, Kowloon, Hong Kong.

Wearable systems integrated with fiber-based electronic and photonic devices are soft, ubiquitous, flexible, stretchable, light, permeable, having the most favorite features of human-friendliness. It is extremely desirable to replace rechargeable batteries or prolong their life by harvesting energy from ambient or our body for the wearable systems to work for us anywhere at any time.

In this paper, our recent progress is presented on a number of issues of fiber-based hybrid energy conversion systems. Theoretical models for the fiber-based piezoelectric, triboelectric and their hybrid generators are proposed and verified to predict the output performance of the devices in terms of materials, device structure, harvesting circuits and operating conditions. The interaction between the cascaded PENG and TENG units in a hybrid nanogenerator and its effect on output are disclosed. Furthermore, the theoretical upper limits of output from contact-mode FTENG are revealed and verified experimentally by considering the electric breakdown due to field-induced- emission and gas- ionization. In addition, an experimental platform developed is reported for reliable triboelectric charge measurement of highly deformable and porous materials like fabrics. An extended triboelectric series is described by us including twenty-one types of commercial and new fibers. On the other hand, fiber-based flexible thermoelectric energy conversion devices are being developed. The materials, fabrication processes and characterization are discussed. The study sheds light on the scope and focus for further improvement of the devices. Based upon the findings, we have made significant enhancements of the performance.

Acknowledgement
The work has been partially supported by Research Grants Council of Hong Kong SAR Government (Grant No. 525113, 15215214, 15204715, 1521016) and Hong Kong Polytechnic University (Grants. 1A-BB3).

References

8:45 AM ES21.08.03
Self-Powered Electronic Medical Devices Zhou Li; Beijing Institute of Nanoenergy and Nanosystem,CAS, Beijing, China.

Recently, piezoelectric nanogenerator (PENG) and triboelectric nanogenerator (TENG) have attracted much attention and been considered as another potential solution for harvesting mechanical energy. With its high output performance, outstanding biocompatibility and low cost, nanogenerator (NG) has been studied for powering implantable medical electronic devices.

Here, we demonstrated an in vivo biomechanical-energy harvesting using a NG. An implantable triboelectric nanogenerator (iTENG) in a living animal has been developed to harvest energy from its periodic breathing. The energy generated from breathing and body moving was used to power a prototype pacemaker and a low-level laser cure (SPLC) system, respectively. It was found that the self-powered system could regulate the heart rate of a rat and significantly accelerated the mouse embryonic osteoblasts' proliferation and differentiation. Real-time acquisition and wireless transmission of self-powered cardiac monitoring data was demonstrated for the first time. It showed broad clinical applications of implantable self-powered medical systems for disease detection and health care. These works are concentrated on live-powered implantable medical devices. The NGs can convert the mechanical energy from human motion into electricity and drive the implanted long-term self-powered medical devices or biosensors. These are significant progress for fabricating implantable self-powered medical electronic devices using NGs as a power source and an active sensor.

Reference :

9:00 AM *ES21.08.04
Triboelectric Nanogenerator for Weak Mechanical Energy Source Yusufan Hu; Peking University, Beijing, China.

Energetic motions like wind and tide are already well handled with existing technologies on large industrial equipment for examples. Meanwhile, mechanical movements with small amplitudes and low frequencies are underexplored, which take place in a wider range of both time and space scales by random excitation in the environment. Fully utilizing such abundant weak energy sources ensures a more powerful and more sustainable self-powered system. However, higher requirements are put forward for weak energy harvesting technologies, especially in two terms of sensitivity and efficiency. Several recent progresses of weak mechanical energy harvesting based on triboelectric nanogenerators are summarized here, including designing the device with unstable mechanical structure, utilizing soft textile to capture subtle body movement, investigating mechanical motion in the system for efficiency optimization, realizing low-loss power management, etc.

9:30 AM ES21.08.05
Triboelectric Nanogenerators for Wearable Physical Monitoring Systems Wei Tang; Beijing Institute of Nanoenergy and Nanosystems, Beijing, China.

There have been profound research works aiming at monitoring humanity physiological signals for disease prophylaxis and treatment, health assessment, tactile (or touch) sensing,
and even security application by developing wearable/portable and sensitive nanogenerator-based sensors. More often, sensors focusing on diagnosis or precaution could meet practical demand by discovering bioelectric signals from special point, such as blood pressure from the radial artery revealing arterial sclerosis, movement of body and eyeballs telling sleep disorder, and motion of respiratory muscles for diagnosis of respiratory disease, respectively. Meanwhile, the foot pressure distribution not only can suggest footwear design and sport biomechanics information, but also indicate possible injury and even predict ulceration in the feet of patients with type 2 diabetes. Specifically, plantar pressure values from a lot of areas, including heel, lateral mid foot, metatarsal, and so on, can serve as a necessary medical indication. In this paper, we present two our recent works on utilizing nanogenerators as the sensing component and then constructing wearable physical monitoring systems for real-time foot pressure mapping and ankle rotation angle sensing. As for the foot pressure mapping, a flexible printed circuit board (FPC) with 32 pieces of PVDF as the PENG pressure sensors (PENG-PS) is employed, which can be large quantity manufactured at low cost. To convert the raw sensor signal to digital signal, the FPC with PENG-PS attached is connected to a designed data acquisition circuit (DAQ). These converted results can be transmitted to mobile terminal, such as laptop, pad, and smart phone through Bluetooth 4.2 protocol, then the real-time pressure distribution is reconstructed. More importantly, through driving by a hybridized triboelectric-electromagnetic nanogenerator, a self-powered and real-time pressure mapping system is demonstrated. As for the ankle rotation angle sensing, a free-standing rotary TENG is utilized. It achieved a rotation resolution less than 1 degree. Moreover, by employing two sets of TENGs, the rotation direction can be detected. We integrated the device with embedded circuits, which can convert the electric signal of TENG into digital data, and transmit to the laptop or smart phone through Bluetooth, forming the real-time monitoring. These works show the promising future of constructing wearable sport monitoring system by utilizing TENG.

9:45 AM BREAK

SESSION ES21.09: Piezotronics III
Session Chairs: Youfan Hu and Zhou Li
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 132 C

10:15 AM *ES21.09.01
Self-Powered Flexible Electronics Beyond Thermal Limits
Koon Jao Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

This seminar introduces three recent progresses of self-powered flexible electronic systems beyond thermal limits. The first part will introduce self-powered systems for IoT sensors and flexible energy source. Flexible nanogenerator converts external bio-mechanical movement into electrical energy for self-powered IoT and biomedical devices such as pacemaker and transportation. In addition, flexible piezolectric materials detects the minute vibration of membrane or human skin that expands the application of self-powered acoustic sensor and healthcare monitor. The second part will introduce laser material interaction for flexible applications. Laser technology of ultra-short pulse duration becomes important for future flexible electronics since high temperature process can be adopted on plastic substrates, which is essential for high performance electronics. Exciting results of flexible laser material interaction will be explored from both material and device perspectives including nanomaterial synthesis, inorganic laser liftoff and plasmonic material realization. The third part will discuss flexible large scale integration (f-LSI) for flexible CPU and high density memory. Flexible LSI is an essential part of future electronics for data processing, storage, and radio frequency (RF) communication. To fabricate f-LSI, we integrated 0.18 CMOS process of single crystal silicon nano-transistors with flexible electronics. Simultaneous roll transfer and interconnection of flexible NAND Flash memory was achieved using anisotropic conductive film (ACF). Finally, we introduce the highly efficient and long-term stable flexible vertical micro LED (f-VLED) for full color displays, wearable and biomedical applications. Using optogenetic mouse models, f-VLED stimulated motor neurons deep below layer III from the brain surface and induced mouse behavior changes. These f-VLED can be also used as tools of skin research and phototherapy.

10:45 AM *ES21.09.02
A Quantum-Mechanical Treatment of Contact Electrification
Morten Willatzen1,2, and Zhong Lin Wang1,2,3; 1Chinese Academy of Sciences, Beijing Institute of Nanoenergy and Nanosystems, Beijing, China; 2University of the Chinese Academy of Sciences, School of Nanoscience and Technology, Beijing, China; 3School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

With the challenge of powering networks of trillions of sensors and devices for the Internet of Things the need for effective generators harvesting low-frequency vibrational energy from the ambient is expected to increase dramatically. This type of energy should be mobile and ubiquitously accessible entailing generators that are compact, effective over a large bandwidth, and of small physical dimensions. Triboelectric nanogenerators (TENGs) are ideal candidates [1] out-competing traditional electromagnetic generators as the latter is ineffective at the low frequencies characterizing ambient vibrational energy from wind, human activity etc. Further, TENGs may provide high power densities up to 500 W/m² or 15 MW/m³. The latter characteristics of TENGs have fuelled a huge interest in exploiting and designing effective generators experimentally. Despite triboelectric energy and charge transport in TENGs is an effect known since ancient times, a detailed microscopic understanding is still not available [2,3].

In this work, we present a quantum-mechanical model of contact electrification between atomic systems and then proceed to analyze the more complicated case involving crystalline solids [4]. The transfer mechanism in atomic systems, that we consider, is based on electron transfer from an atomic state with energy Eᵢ to a lower-energy (Eⱼ) state associated with material B and the emission of a photon with energy Eᵥ + Eᵥ. The spontaneous emission rate is determined using Fermi’s Golden Rule in the dipole approximation based on the one-electron Schroedinger equation. The process requires spatial overlap of the initial and final state wavefunctions, hence the electron transfer is a sensitive function of the distance between the two materials A and B as well as the symmetries of the atomic states. We start out by determining the spontaneous emission rate for a fixed distance between atoms and then analyze the temporal variation of level occupations, i.e., the time dependence of electron transfer, using the Einstein rate equations and assuming the higher-energy level is occupied initially. Next, we determine the transfer of electrons in a dynamic setup where the distance of the two materials changes in an oscillatory manner.

Inspired by this simple quantum-mechanical description of contact electrification between atomic systems we generalize the idea to crystalline solids. Using a one-band k.p envelope function approximation of electronic states [5], the dipole matrix elements between surface states in dielectric materials A and B are computed. Since solids are quasi-continuum systems the transfer rate depends intrinsically on the conduction and valence bands of the two interacting materials, Fermi levels of the two materials, temperature, the vacuum energy (since vacuum separates the two materials), effective masses, and the distance between materials A and B. We calculate the spontaneous emission rate as a function of distance by varying the Fermi levels, temperature, and the effective masses. The model can easily be generalized to describe contact electrification between conductors and/or dielectrics. Other transfer mechanisms such as phonon emission through, e.g., the Froehlich coupling can be described in a similar way.

References

11:15 AM *ES21.09.03
Universal Approach of Enhancing Piezotronics by Creating Pores in Piezoelectric Semiconductors Chuan-Pu Liu1, Kapil Gupta1, Yu-Lun Su1 and Ruesy-Chi Wang2; 1National Cheng Kung University, Tainan, Taiwan; 2National University of Kaohsiung, Kaohsiung, Taiwan.

In the Internet of Things era, both self-powered nanodevices and nanogenerators (NGs) that harvest energy from mechanical vibrations are highly attractive, prompting a rapid surge in research on enhancing their performance. To this end, it becomes nature to search for new materials with higher piezoelectric coefficients. However, it is not always a simple task to fabricate large-scale and high-quality new materials as considering the limited synthesis techniques. Alternatively, to optimize the microstructure characteristics of a given material may be more beneficial and effective. To alter the properties of a given material, we have demonstrated several strategies including doping, oblique orientation and alloying and the output performances of various piezotronic devices as well as piezoelectric nanogenerators have been significantly improved. However, some of the strategies are specific to materials and those material-dependent characteristics may have limitations for universal utilization. We demonstrate a versatile approach for diverse materials, by altering microstructure with discontinuous nano-pores in one-dimensional nanostructures, which can be readily extended into higher-dimensional single crystal materials, such as epitaxial thin film. This novel approach is demonstrated for two applications, i.e., direct-current (DC) NGs and piezotronics by taking ZnO as a model, where remarkably enhanced performance is depicted in theoretical simulations and confirmed by experiments. Here, we report that porous ZnO nanowires-based DC-NGs demonstrate ~23 times enhancement in output performance, and strain-gated transistors exhibit ~6 times enhancement in force-sensitivity. This can potentially augment energy harvesting and pressure sensing for many applications, such as, self-powered nano-devices and touch-panels.

11:45 AM ES21.09.04 Porous Polymer Thin Films for Mechanical Energy Harvesting and Self-Powered Electronics Yanchao Mao; MOE Key Laboratory of Materials Physics, School of Physics and Engineering, Zhengzhou University, Zhengzhou, China.

Triboelectric nanogenerators (TENGs) are promising innovative energy conversion devices that convert mechanical energy to electricity based on triboelectric friction. We developed a series of TENGs based on sponge-like porous polymer thin films such as polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE). The porosity effect on the output performance of the porous TENG was investigated under mechanical impacts. The output voltage of the porous TENG is obvious higher than that of the solid polymer thin film based TENG under the same condition. The porous TENG can also generate considerable electricity by harvesting mechanical energy from human motions. The generated electric energy could instantaneously power some light emitting diodes (LEDs) and other small electronics without any energy storage process. The development of the porous TENG could open a new avenue toward developing self-powered personal electronics, owing to their flexibility, simple structure, and the ability to harvest mechanical energy from human motions.

References:

SESSION ES21.10: Piezoelectric and Triboelectric Nanogenerators V
Session Chairs: Dongseok Suh and Jun Zhou
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 132 C

1:30 PM *ES21.10.01 Optimized Interface Conditions for Piezoelectric and Energy Harvesting Potential in ZnO Juergen Roedel and Till Frömling; Earth and Materials Science, Technische Universität Darmstadt, Darmstadt, Germany.

The coupling between piezoelectric and semiconducting properties opens the pathway to the development of electronic devices with additional functionality. [1] In the past, the changes in potential barrier, which were achieved via application of mechanical stress, are only in the order of meV or a few percentage of the total height of the potential barrier. Similarly, charge screening is deemed critical and not necessarily the full piezoelectric potential of ZnO can be harvested.

The latter is addressed by conducting an experimental study using undoped intrinsically conductive ZnO single crystals with both Ohmic and Schottky contacts [2]. The effective piezoelectric response is then quantified at temperatures from -140°C and 20°C, and frequencies from 0.5 Hz to 160 Hz. The formation of an electrostatic potential barrier at the metal-semiconductor interface was found to increase electrical resistance and hence delivers full utility of unbiased piezoelectric coefficients of ZnO single crystals even at room temperature. This can also be seen as an illustration and quantification of the piezotronic effect on an ideal macroscopic single crystal. Due to the Schottky barrier the piezoelectric charge cannot be fully screened by electronic charge carriers.

An almost complete elimination of the potential barrier at the interface was achieved by utilizing a bicrystal ZnO / ZnO interface with well-defined polarization conditions. The methodology is based on bonding two well-aligned single crystals of ZnO with an intermediate thin polycrystalline sacrificial layer of doped ZnO. Subsequent high temperature growth treats the single crystals into the sacrificial layer and consumes the polycrystalline materials either partially or fully. The doping content is optimized so that a double Schottky barrier develops at the ZnO-ZnO interface. For full growth, a single interface evolves. Based on this structure, we will show how stress can tune the potential barrier in head-to-head and tail-to-tail orientation of the polarization vector to enhance/lower the conductivity across individual ZnO bicrystal interfaces. Surpassing the stress sensitivity of previous piezotronic systems. [3]


2:00 PM ES21.10.02 A Biomimetic Pressure Sensor Based on Ultrathin Supercapacitor and Flexible Triboelectric Nanogenerator Xia Cao1; Jingdian Zou1, Meng Zhang1, Ning Wang2 and Zhong Lin Wang1; 1Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China; 2University of Science and Technology Beijing, Beijing, China.

With the fast development of supercapacitor and triboelectric nanogenerator (TENG), it is now possible to fabricate biomimetic pressure sensors with high flexibility and sustainability. Herein, an ultrathin supercapacitor is fabricated with the paper sheet and the solid electrolyte for storing energy generated by TENG. With a sandwich design, the triboelectrets sandwiched within the two solid supercapacitors can not only store electrical energy by a wireless energy transfer mode but also help TENG imitate the receptor’s
unique characteristics by simultaneously measuring both static and dynamic pressures in a self-driven mode. The linear detection range of dynamic pressure is from 1 to 4 N cm⁻² with a sensitivity of 17.5 V cm⁻² N⁻¹ and a detection limit of 0.3 N cm⁻². The detection range of static pressure is from 0.5 to 4 N cm⁻² with a sensitivity of 12.1 mV cm⁻² N⁻¹ and a detection limit of 0.07 N cm⁻². In addition, the voltage of the supercapacitor increases linearly with the vibration times, which hints that this integrated device also endows functions such as vibration counting and frequency computing. This work contributes to new strategies for making multifunctional biomimetic electronics that promote the development of artificial intelligence.

2:15 PM *ES21.10.03 Design and Energy Application of Piezoelectric Biomaterials Rusen Yang; School of Advanced Materials and Nanotechnology, Xidian University, Xian, China.

Multifunctional materials have received increasing attention in recent years. Owing to their inherent biological nature as well as piezoelectric properties, piezoelectric biomaterials are considered as promising candidates for application in fields ranging from electrochemical energy storage to biological systems. The rational material design is important to enhance their piezoelectric and biological activity. Herein, recent advancements to piezoelectric biomaterials like peptide-based micro/nanostructures are provided. Synthetic methods, morphological features, and piezoelectric performance of piezoelectric biomaterials are presented. The effect of growth direction, phase and structure of piezoelectric biomaterials on their piezoelectric activity are discussed. The applications of piezoelectric biomaterials in the field of nanogenerators are provided at the end.

Reference:
1. H. Yuan, T. Lei, Y. Qin, R. Yang, Flexible electronic skins based on nanogenerators and piezotronics, Nano Energy, submitted

2:45 PM ES21.10.04 Structural Design of Triboelectric Nanogenerator for Harvesting Environmental Mechanical Energy and Self-Powered Motion Sensing Yannan Xie; Nanjing University of Posts and Telecommunications, Nanjing, China.

Aiming at environmental renewable and sustainable energy sources, energy harvesting technology has been developing rapidly in the recent years. Emerging as significant applications of Maxwell’s displacement current in the energy field, triboelectric nanogenerator (TENG) has received worldwide attention and undergone speedy progress. In the field of TENG, structural design is an important research topic due to the diverse application circumstances. In our works, several device structures have been carefully investigated, including angle-shaped wind-driven TENG with enhanced output performance and very low start-up wind speed, kinesio-tape based TENG with compact structure for self-powered human motion sensing, and so on. We will also discuss the applications of TENG as flexible electronics for wearable device. Our works may provide design strategies for TENG and put forward its practical applications as newly energy harvesters and self-powered sensors.

3:00 PM BREAK

SESSION ES21.11: Piezoelectric and Triboelectric Nanogenerators VI
Session Chairs: Jürgen Roedel and Yunlong Zi
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 132 C

3:30 PM *ES21.11.01 Boosting the Output of Energy Conversion from Evaporation Driven Water Flow in Porous Carbon Film Jun Zhou; Huazhong Univ of S&T, Wuhan, China.

Harvesting energy from the environment offers great promise for the application of distributed sensor networks. Ideally, highly effective energy conversion processes should be environmentally friendly, spontaneous and maintenance-free. Recently, we have reported that evaporation-driven water flow within a porous carbon film can reliably generate sustainable electricity with open-circuit voltage (Voc) up to 1 V and short-circuit current (Io) of 100 nA, respectively[1]. The output performance of the device can be easily scaled up by using all print method[2]. A device based on freestanding and flexible carbon-based hybrid film with size of 400*450*0.13 mm³ produces an Io ~ 28 μA [3]. The Voc of the device can be tuned from -3 V to 3 V by manipulating the surface functional groups on the carbon nanoparticles. In addition, a hybrid energy utilization technology was also developed by using solar energy for desalination (solar thermal efficiency of ~75%) and extracting electricity (power of ~ 1 W m⁻²) from the evaporation induced salinity gradient [4]. Because of the ubiquity of water evaporation in nature and the low cost of materials involved, our study presents a novel avenue to harvest ambient energy and has potential applications in low-cost, green, self-powered devices and systems[5-6].

Reference

4:00 PM *ES21.11.02 Piezoelectric Energy HARVESTER Having a Wireless Communication Capability Without a Battery Demonstrated by the Piezoelectric Single Crystal PMN-PT Dongseok Suh¹, Yourack Lee¹, Jeong-Ho Lee², Sang-Goo Lee³ and Yong Sin Kim³;¹Sungkyunkwan University, Suwon-Si, Korea (the Republic of);²iBule Photonics Co. Ltd, Incheon, Korea (the Republic of);³Korea University, Seoul, Korea (the Republic of).

We have examined the piezoelectric single crystal PMN-PT (Pb(Mg1/3Nb2/3)O3-PbTiO3) as a piezoelectric energy harvester to convert the mechanical energy to electrical energy in various forms. One of those applications is the push-button-type energy harvester, which can directly generate the electrical energy enough to send a wireless signal to the nearby receiver without battery. The quantitative analysis of the voltage and the power generation during the push-button operation had been done, and it could be doubled when we employed the idea of snap-through buckling. The other is the vibration energy harvester that is designed for the status-monitoring purpose of a pole-mounted electrical power transformer. From the basic vibration originating from the AC voltage, it could permanently generate the electricity required for operating an event logger of partial discharge and sending the wireless message containing that data. From those two works, we demonstrate that the piezoelectric single-crystal PMN-PT can be one of the most reliable and powerful materials for the piezoelectric power generation combined with wireless communication capability. (This project is supported by the Korea Electric Power Corporation (KEPCO).)

4:30 PM *ES21.11.03
Standardization of Triboelectric Nanogenerators—Progress and Perspectives

Yunlong Zi; Mechanical and Automation Engineering, The Chinese University of Hong Kong, Shatin, Hong Kong.

The rapid development of the Internet of Things (IoT) and the increasing energy crisis call for a new type of energy sources. Triboelectric nanogenerators (TENGs), which can convert mechanical energies to be electricity, develop quickly in recent years and catch more and more people’s eyes in the world. Meanwhile the importance of the standardization for TENG has been emphasized, and developing the standardized theoretical models and experimental methods to evaluate the performance quantitatively becomes more and more important for the commercialization and industrialization of the TENG technology. This presentation will systematically review the origin of the V-Q plot based standardized characterization methods and the figure-of-merits (FOM) based the standard for quantitatively characterizing the energy output. This presentation will also discuss several essential factors, including the input energy, environmental factors, and life-time assessment, to be potentially involved in standards for TENGs in future. The standardization of TENG will greatly helpful to understand and improve this emerging energy harvester towards further applications. We believe the standardization of TENG will greatly facilitate the commercialization and industrialization of TENGs in future.

SESSION ES21.12: Nanogenerators and Piezoelectricity

Session Chairs: Kourosh Kalantar-zadeh and Wenzhuo Wu

Friday Morning, April 26, 2019

PCC North, 100 Level, Room 132 C

8:30 AM ES21.12.01

Computation of Electronic Energy Band Diagrams Applied to Piezotronic Photoelectrochemical Electrodes

Lazarus N. German1, Yanhao Yu1,2, and Xudong Wang1, Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States; 2School of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts, United States.

Photoelectrochemical (PEC) reactions are a promising pathway for the direct transformation of solar energy to chemical fuels.1–3 The past decade has produced significant progress in PEC reactions for this type of conversion, especially PEC water splitting for H2 generation.4–6 Despite these advancements, the ultimate industry-level solar-to-hydrogen productions through PEC still remains unreachable due to challenges in the stability, light absorption and charge separation.7 In regards to charge separation, the piezotronic effect has arisen as a new paradigm to break the forgoing capstone. Applying ferro- and piezoelectric materials an their polarization trigger considerable free carrier redistribution in the adjacent semiconductor. As a result, the charge separation and overall PEC performance can be effectively tuned.

Electronic energy band diagrams provide useful and illustrative information on how materials stacking might affect electronic properties and charge transport throughout a multi-junction device. However, schematic diagrams, which are often used in many publications, lack quantified changes in potential across junction interfaces. This is especially true as the energetics become increasingly untuitive when incorporating the effects of dielectric layers and applying ferro- and piezoelectric dipoles, such as the case of piezotronics. By applying the Poisson-Boltzmann equation and idealizing interfaces, we can produce first approximation, quantitative electronic energy band diagrams for solid/solid and solid/electrolyte heterojunctions that incorporate ferro- and piezoelectric elements.8 Using a Mathematica code that we developed, we can show that band bending at semiconductor/electrolyte interface can vary over several meV by adjusting piezotronic polarization.

Aside from the semiconductor/electrolyte interface, piezoelectric have also shown great promises in promoting the efficiency of PEC devices by other means. Full-gear functionalities of these devices are constrained by the longstanding contradiction between the charge collection of semiconductors and the screening effect of polarization materials. We tackled this issue by decoupling the collecting and screening trajectories using graphene as the charge collector.9 The moderate charge density of graphene ensures minimal screening of the adjacent electrical polarizations and concurrently delivers photogenerated free carriers toward the counter electrode. Based on a PMN-PT/graphene/TiO2 piezotronic PEC system, substantial performance gains were received through tuning the interfacial electronic energy level via ferroelectronic polarizations, obtaining a favorably shifted onset potential. Both calculation and experimental results suggest that this outcome was beneficial from the low screening effect from graphene. In contrast, a gold electrode will fully screen the polarization from PMN-PT and yield similar PEC performance despite of the polar conditions. This work reveals graphene could be an ideal conductive electrode selection for free piezoelectric PEC devices from the performance capstone imposed by the trade-off between carrier collecting and charge screening.

References:


8:45 AM *ES21.12.02

Energy Harvesting by Triboelectric Nanogenerators for Self-Powered Sensing Systems

Guang Zhu1,2 and Zhong Lin Wang1,3; 1Beijing Institute of Nanoenergy and Nanosystems, CAS, Beijing, China; 2University of Nottingham Ningbo China, Ningbo, China; 3Georgia Institute of Technology, Atlanta, Georgia, United States.

Converting ambient mechanical energy into electricity provides a viable solution to a sustained power source for distributed small electronic devices. It is particularly significant for the development of wireless sensor networks. In the past five years, we innovatively utilized contract electrification on the surface of flexible thin-film materials, proposing a new mechanism to convert mechanical energy to electrical energy through triboelectric conversion. This so-called triboelectric nanogenerator (TENG) has been developed for the past decade and attracted more and more research interest. However, the high performance of TENG is largely constrained by the low energy density of the piezoelectric nanogenerators. This work introduces a new approach to converting mechanical energy into electrical energy, and we will discuss the origin of this phenomenon. The mechanical energy conversion efficiency of the proposed energy harvester can be evaluated by the power density, which is calculated by the output voltage and current. The experimental results suggest that the proposed TENG can harvest energy from various mechanical sources with high energy conversion efficiency. This technique opens the door to the development of new energy harvesting devices for self-powered sensing systems.

9:15 AM *ES21.12.03

Ferroelectric and Piezoelectric Control of the Optical Properties of Advanced Materials

Yang Zhang1, Weining Jie1, Ping Chen1, Weimei Liu1 and Jianhua Hao2; 1Nankai University, Tianjin, China; 2The Hong Kong Polytechnic University, Hong Kong, Hong Kong; 3Sichuan Normal University, Chengdu, China.

Piezoelectric and ferroelectric materials have shown great potential for control of the optical process in emerging materials. There are three ways for them to impact on the optical process in various materials. They can act as external perturbations, such as ferroelectric gating and piezoelectric strain, to tune the optical properties of the materials and devices. Second, ferroelectricity and piezoelectricity as innate attributes may exist in some optoelectronic materials, which can couple with other functional features (e.g., semiconductor transport, photocexcitation, photoactivities) in the materials giving rise to unprecedented device characteristics. The last way is artificially introducing optical functionalities into ferroelectric and piezoelectric materials and devices, which provides an opportunity for investigating the intriguing interplay between the parameters (e.g., electric field, temperature, strain) and the introduced optical properties. Herein, the tuning strategies, fundamental mechanisms, recent progress in ferroelectric and piezoelectric effects modulating the optical properties of a wide spectrum of materials, including lanthanide-doped phosphors, quantum dots, two-dimensional materials, and wurtzite-type semiconductors are presented. The future outlook and challenges of this exciting field are suggested.

9:45 AM BREAK
Chip-based 3D subdiffraction microscopy with easy-configuration, fast-speed is highly desired. We propose wide-field far-field super-resolution imaging chip based on frequency shift effect. Our previous work demonstrates wide-field label free super-resolution imaging can be achieved utilizing a combination of a spatial frequency shift and a Stokes frequency shift [1, 2]. Recently, combining the broad spectra of polymer fluorescent film and well-designed polygon shape, full-angle wide wave vector coverage illumination was achieved for complete imaging reconstruction to eliminate distortion. By frequency shift and iteratively stitching different spatial frequency range together in Fourier space, reconstruction of two dimensional (2D) samples without distortion was achieved in a wide FOV. Furthermore, frequency loss free 3D super-resolution circuits was designed. The spatial-frequency of surface wave illumination can be tuned flexibly through wave vector modulation and operation, to achieve complete spatial-frequency detection for deep subwavelength imaging. Piezophotonic effect can be used to precisely control the phase and frequency shift in the circuit.

References:

Piezoelectricity and Ferroelectricity in Nylons for Energy Harvesting
Sailem Arwa1, and Kamal Asadi1; 1Max Planck Institute for Polymer Research, Mainz, Germany;
2School of Chemical & Materials Engineering, National University of Sciences & Technology, Islamabad, Pakistan.

Research on piezoelectric polymers is mostly concentrated on polyvinylidene difluoride, PVDF, and its random copolymers, poly(vinylidene difluoride-trifluoroethylene), P(VDF-TrFE). Among engineering polymers, odd-nylons are ferroelectric. Since the discovery of ferroelectricity in polymers, nearly half a century ago, a solution processed ferroelectric nylon thin-film has not been demonstrated due to the strong tendency of nylon chains to form hydrogen bonds. In this contribution, we show that solution quenching allows for the fabrication of ultrathin and optically transparent nylon-11 thin-films which are crystallized in the polar piezoelectric/ferroelectric phase. The ferroelectric properties are on-par with those of PVDF and P(VDF-TrFE). However, nylon ferroelectric capacitors show superior fatigue-free behavior upon cycling in sharp contrast to PVDF and P(VDF-TrFE) capacitors.

Nylons are among the basic materials for textile industry. Hence realization of piezo/ferroelectricity in nylon fibers can readily lead to textiles that are responsive to electrical or mechanical stimuli, thereby enabling e- or smart textiles. We discuss fabrication of piezoelectric nylon fibers and nanogenerators thereof for energy harvesting.

Electromechanical Response of Few-to-Monolayer SnS PVDF-Grown on Flexible Mica
Naoki Hiragashita, Hayami Kamamoto and Kosuke Nagashio; The University of Tokyo, Tokyo, Japan.

Two-dimensional orthorhombic SnS has been recently attracted interests in the application to nanogenerators for its remarkable piezoelectric coefficient, \( d_{145} \) nm/V, for monolayer, which is much larger than MoS\(_2\), and comparable to PZT [1]. However, there has not been demonstrated any observation of piezoelectric response for SnS, because strong interlayer bonding by lone pair electrons in Sn atoms prevents the mechanical isolation of monolayer [2]. We have successfully realized the growth of few-to-monolayer SnS on mica substrate via physical vapor deposition (PVD), where the growth temperature was precisely controlled to balance adsorption/desorption of SnS. Synthesis mica, KMg\(_3\)Al\(_2\)O\(_6\)F\(_2\), is an attractive platform with atomically flat surface, thermal tolerance up to 1100°C, and flexibility, which enable a straightforward process from crystal growth to fabrication of flexible devices. In this work, for the first time, electromechanical response of SnS is demonstrated with using ultra-thin SnS layers grown on mica. SnS is a semiconductor piezoelectric unlike the traditional piezoelectric ceramics; therefore, understanding of piezoelectric effect in SnS is essential as well as piezoelectric effect, toward the nanogenerators application. In order to observe the piezoelectric effect, electromechanical response was investigated for ~10 layers SnS, which is supposed to be non-piezoelectric. Flexible device was fabricated with PVD-grown SnS on mica substrate directly bonded to PC or PET film. \( L_0 \)-time measurements at constant \( V_0 \) were performed with applying in-plain tensile/compressive strain of \( \varepsilon \sim \pm 0.5 \% \) respectively. Electrostatic responses were observed reproducibly; the resistance \( R \) increased with tensile strain and decreased with compressive strain. These results are consistent with the theoretical study on bandgap \( E_g \) of SnS with different strain, \( E_g \) increases with tensile strain and vice versa [3]. Based on these piezoelectric responses, the typical gauge factor was estimated as \( \Delta R/R = 1.24 \), which is comparable to that of metals. The present SnS on flexible mica platform will be able to extract the piezoelectric effect for monolayer SnS with negligible noise level.


Intrinsic Energy Conversions for Photon-Generation in Piezo-Phototronic Materials—A Case Study on Alkaline Niobates
Balong Huang; The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

The creations of photons in response to mechanical stimuli in a crystal that has noncental symmetry are the great fundamental physics responsible for numbers of important technologies. The underlying mechanism and complete theory for a precise explanation of the mechanical-photonic energy conversion phenomena is vital important. We take commercial piezoelectric LN\(_\text{iMnO}_3\) (LiMNO\(_3\)) crystals as the example to interpret the detailed mechanisms of energy conversions for the photon-generation through a native point defects study. It was found the Frenkel and Schottky type complex pairs as well as the antisite pair defects acting as energy harvesting and migration centers, which are very easy to form and active. It does to be the extra deep electron or hole traps levels near the valence or conduction band edge, respectively. That is the substantial energy reduction via a spontaneous exchange effect by them to continuously collect and transport host charges along the path via localized states to the deep recombination levels. The initiating energy barrier is small.

In Vivo Implanted Battery-Free Direct-Current Micro-Power Supply from In Vivo Breath Energy Harvesting
Jun Li, Lei Kang, Yin Long, Hao Wei, WeiBo Cai and Xudong Wang; University of Wisconsin–Madison, Madison, Wisconsin, United States.

Majority of current IMDs are powered by conventional surgical or technical batteries that contribute up to 90% weight and volume of the entire device. [1,2] While replacement of or recharging the batteries requires conventional surgical or technical efforts, introducing additional suffering and complexity to the patients, other battery potential issues such as overheated and leakage of toxic electrolyte further prohibit the advancement and miniaturization of IMDS. Therefore, increasing efforts are now being focused on the innovation of designated IMD power sources. Implantable nanogenerators (i-NGs) have been designed to convert biomechanical energy into electricity. [3,4] In spite of their numerous merits, the outputs of state-of-the-art i-NGs are always in a form of largely discrete pulses. Although their theoretical output power could be sufficient for IMDS, battery component is still needed in the i-NG design to produce a steady and usable direct current (DC) output. Moreover, most i-NGs are non-stretchable with incompatible mechanical properties compared to soft biological tissues, which further challenges their practical application.

In this work, we reported an ultra-soft stretchable i-NG system that could function as a battery-free DC micro-power supply. The i-NG consisted of ultrathin micro-scale interdigital electrodes (IDES) and multi tribo-active layers with a small working area (approximately 2 cm\(^2\)), packaged with biocompatible silicone elastomer. While the micro IDES support the output of high frequency electricity (1 \( \mu \)A at 70 Hz) driven by slow mechanical stimulation, the silicone elastomer and an embedded cavity design enable i-NGs with extremely low Young’s Modulus (46 kPa), exactly matching the mechanical property range of most soft biological tissues. By implanted inside the abdominal cavity of Sprague Dawley (SD) adult rats, the i-NG could convert slow diaphragm movement during normal breath into stable high-frequency electrical spikes, which were readily transmitted into a continuous –2.2 V DC output on a LED load after being integrated with a basic electrical circuit (rectifier and capacitor) for a relatively long period of time.
This electric output could continuously power the LED without any observable power decay, successfully demonstrating a constant operation of small electronics DC power free of the battery component. This solely biomechanical-energy driven DC micro power supply offers a very promising solution for the development of self-powered IMDs in the near future.

References:

11:45 AM ES21.12.09
Triboelectric Nanogenerators as Soft Power Sources Xiong Pu; Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China.

Rapid advancements in stretchable/multifunctional electronics impose the challenge on corresponding power devices that they should possess comparable flexibility, stretchability and functionalities. In this talk, we briefly summarize our recent progresses on wearable energy harvesting devices, especially triboelectric nanogenerators aiming to power soft electronic skins or soft electronics/robotics. We report a soft skin-like triboelectric nanogenerator that enables both biomechanical energy harvesting and tactile sensing by hybridizing elastomer and ionic hydrogel as the electrification layer and electrode, respectively. Ultra-high stretchability and transparency are achieved simultaneously for an energy-harvesting device. Lastly, we report our updated progresses on and self-healable soft TENGs by utilizing self-healable elastomers. Bulk thin layers of conductive polymers are achieved by transfer the film onto pre-strained self-healable elastomers, which later ensure the realization of self-healing, stretchability, and transparency of the TENG simultaneously. Our work provides new opportunities for soft power sources and potential applications in soft/wearable electronics.

SESSION ES21.13: Nanogenerators and Piezotronics III
Session Chairs: Qing Yang and Guang Zhu
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 132 C

1:30 PM ES21.13.01
Boosting the Energy Conversion Efficiency of a Combined Triboelectric Nanogenerator-Capacitor Jin Poo Lee¹, Jae Won Lee¹, Bo-Kyung Yoon¹, Hee Jae Hwang², Sungwoo Jung¹, Katherine A. Kim¹, Dukhyun Choi¹, Changduk Yang¹ and Jeong Min Baik¹; ¹Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of), ²Kyung Hee University, Yongin, Korea (the Republic of).

With the growing popularity of various internet of things sensors and portable devices, such as smartphones and smartwatches, the demand for power generation sources for driving such electronic devices is becoming increasingly important and challenging. If we rely on batteries to drive all of the sensors related to Internet of things, most of the IoT would be impossible. Here, we report the exciting possibilities for the use of triboelectric nanogenerators (TENGs) toward real-time self-powered electronics, such as a smartphone-to-smartwatch telecommunication over Bluetooth via the capacitors charged by the TENGs, a self-powered pulse sensor, and a real-time self-powered calculator. To achieve the high-output power of the TENGs, we focused on multiple strategic points such as device structures, contacted materials, and mechanical systems, as well as circuit design methods of enhancing the charging efficiency to the energy storage device. The novel integration scheme of TENGs made it generate areal output power of approximately 3 mW/cm² under a low frequency of 3 Hz through a gear-cam system. Based on these results, fast-chargeable portable power-supplying systems for the continuous self-powered electronic systems were successfully developed.

1:45 PM ES21.13.02
A Novel Triboelectric Nanogenerator Based on Electrospun Polyvinylidine Fluoride Nanofibers for Effective Acoustic Energy Harvesting and Self-Powered Multifunctional Sensing Haiwu Zheng¹ and Yunlong Zi²; ¹Henan University, Kaifeng, China, ²The Chinese University of Hong Kong, Hong Kong SAR, China.

Acoustic energy is mostly wasted with out a proper energy harvesting approach. In this work, an integrated triboelectric nanogenerator (TENG) with a polymer tube is constructed to harvest acoustic energy from the environment, which can work stably in the frequency ranging from 20 Hz to 1000 Hz. The TENG is based on electrospun polyvinylidene fluoride (PVDF) nanofibers and two conductive fabrics. The unique structure design facilitates acoustic energy capturing and the enhancement of sound pressure. The TENG can deliver an open-circuit voltage and short-circuit current of 400 V and 175 μA, respectively, with instantaneous maximum output power density of 7 W/m² under a sound frequency of 170 Hz and sound pressure of 115 dB. The TENG can be used for audio frequency analysis and noise detection. Furthermore, self-powered active sensors are demonstrated for detecting sound source direction and motion velocity of an object making sounds. This work not only provides a simple, cost-effective approach for fabricating high performance TENG to recycle ambient noise energy into available electricity, but also enables self-powered sensing applications, with potential applications in military surveillance, artificial intelligence, Internet of Things, and jet engine noise reduction.

2:00 PM ES21.13.03
Remarkable Output Power Enhancement of Sliding-Mode Triboelectric Nanogenerator Through Direct Metal-to-Metal Contact with the Ground U Jeong Yang and Jeong Min Baik; Material Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Triboelectric nanogenerator (TENG) is one of alternative energy harvesting technologies of ambient mechanical energy source in nature environments. Here, a new-type of sliding-mode TENG with the enhanced potential through the direct metal-to-metal contact with the ground connection is reported. When the positively charged Al layer is contacted with the grounded Al, the electrons flow is promoted to the ground by large potential difference between the two metals. This induces the charge transfer between bottom electrodes, enhancing the electric potential, confirmed by the COMSOL simulations. This new type of TENG generates a maximum power of 0.13 W under low frequency of 3 Hz on an external load of 1 MΩ, corresponding to energy conversion efficiency of approximately 42 %. Performance of the working-mode are also systematically investigated in free-rotating disk-type and patch-type TENGs, which offered a lot of convenience and feasibility for energy harvesting from the wearable energy sources.

2:15 PM ES21.13.04
Mechanically Induced Light Generator Based on Doped Piezophotonic Quaternary Oxysulfide Dengfeng Peng; Shenzhen University, Shenzhen, Alabama, United States.

Piezoelectric semiconductor with optical, electrical and mechanical multifunctions has great potential applications in future optoelectronic devices, the rich physics and applications origin from the intrinsic structures and inner coupling effects. Here, we report that lanthanide ions doped piezoelectric quaternary oxysulfide semiconductor CaZnOS show strong light emission induced by dynamic mechanical stress, the emission is bright enough to see by the naked eyes even under the day light. We design the mechanically induced light generator by embedding the doped CaZnOS powder into the flexibly transparent polymer with good mechanical repeatability. The flexible light generator has a broad range of applications, such as advanced display, stress sensor and information safety.

Reference:
Polymeric piezoelectric nanogenerators (PNGs) have emerged as a suitable candidates to harvest waste mechanical energy to power up portable electronic devices. Smart textiles, with piezoelectric functionalities integrated in the fabrics have been envisioned. In this regards, numerous piezoelectric (nano-)generators based on PVDF or PVDF-TrFE nanofibers have been reported.

However, the piezoelectric polymer (nano-)generators have typically shown low output energy densities; A the common issue hindering their application. Introduction of porosity into the piezoelectric polymer has been proposed to increase the voltage output of PNGs. However, designing a process that allows introduction of pores in polymer fibers with typical diameter of the order 100 nm, would be a breakthrough in the field of PNGs. In this contribution, we discuss an elegant approach to tailor porosity in electrospun P(VDF-TrFE) nanofibers. The approach is based on the thermodynamics of polymer solutions, and solvent/non-solvent interactions with the polymer. We calculated the ternary phase diagram of P(VDF-TrFE)/non-solvent (water)/solvent, and experimentally verified it. Based on the phase diagram, a conscious amount of water is intentionally added into the P(VDF-TrFE) solution to induce porosity in the fiber. PNGs based on the porous electrospun P(VDF-TrFE) nanofibers show systematic increases of the output voltage with porosity. The output power increased from 0.1 mW/cm$^2$ for PNGs with zero porosity to 7 mW/cm$^2$ for PNGs with 50% porosity. Dielectric spectroscopy of the nanofibers attributes the enhanced output to the reduced dielectric permittivity of the fibers and that the voltage generation in the porous fibers is of the same origin as in neat piezoelectric P(VDF-TrFE) films and is due to the relaxation of segments within the restricted amorphous phase.

The triboelectric nanogenerator (TENG) has been investigated intensively during the last decade in terms of power improvement and application as sensors. However, its voltage is usually too high and spike-like to be used directly as a power source for electronic devices. Although there was an effort to adjust the voltage through the circuit design, the circuit board has limitations in the complexity and the bulkiness. Here, we propose a simple approach to change the spike-like voltage profiles to the square-like profiles and adjust the output voltage to be in the suitable range for electronics. We used printed ion gel electrolyte patterns as capacitors and investigated the effects of the dimension of the capacitor, the connection types (serial, parallel) of multiple capacitors, and the electrochemical conditions. The voltage profile of the TENG-ion gel system was modulated by the contact frequency applied to the TENG, the contact area of the ion gel with the electrode, the type of ions in the electrolyte, reduction/oxidation reaction in the gel, and the connection type (parallel, series) between ion gel patterns. We successfully demonstrated the light emission of a large number of printed electrochemiluminescence patterns.

The development of wearable electronics, implantable devices and internet of things put forward an ever-growing demand on distributed power supply, providing an opportunity for technologies that can harvest energy locally from environment. As a promising energy harvesting technology, triboelectric nanogenerators (TENGs) show merits of easy fabrication, low cost, abundant choice of structures and materials compared with other energy harvesting technologies. The working principle of the TENG is based on the conjugation of triboelectrification and electrostatic induction and its theoretical fundamental can be derived from the Maxwell's displacement current.

The practical application of TENGs imposes a challenging requirement to improve the power density of the device, which is highly related to the charge density because it has a quadratic dependence on the charge density. The enhancement of the charge density is restricted mainly by two issues for normal TENG devices under certain intensity of contact or rubbing. The first one is the triboelectrification capability of tribomaterial pairs with certain surface topographies, and the other is the discharge caused by air breakdown. In previous studies, great efforts have been conducted to improve the charge density, based on material selection, structure optimization, surface modification or environment control. The corona charging is a relative facile method that is widely adopted, which can inject charges into dielectric films to enhance the charge density from under 100 μC m$^{-2}$ to about 240 μC m$^{-2}$. However, the injected charges are not stable and the dielectric materials are restricted to electrets. High vacuum environment can suppress air breakdown, which can greatly enhance the charge density to 660 μC m$^{-2}$ for Cu versus polytetrafluoroethylene (PTFE), and 1003 μC m$^{-2}$ with an extra ferroelectric barium titanate (BT) layer. Still, this method is restricted by high requirements of device packaging.

To develop a facile and universal method to enhance the charge density of TENG devices, an integrated self-charge-pumping TENG (SCP-TENG) device with features of floating layer structure and charge pumping is proposed in this work. Derived from normal TENGs, the proposed device adopts a floating layer to store and bind charges for electrostatic induction, while a TENG based charge pump is designed to continuously pump charges into the floating layer at the same time. The SCP-TENG can operate like normal TENGs, while accumulating bound charges with high efficiency to ultrahigh effective surface density of 1020 μC m$^{-2}$ in ambient conditions, which is about 4 times of that of the density corresponding to air breakdown and has potentials to be further elevated in the future. More importantly, this method is rather facile and robust compared to other charge density enhancing approaches, providing an important strategy to achieve ultrahigh-performance for TENG devices, which is crucial for various practical applications ranging from wearable electronics to blue energy.
Advances in next-generation soft electronic devices rely on the development of highly deformable, and healable energy generators to power these electronics. Triboelectric nanogenerators (TENG) have emerged as a promising power source for portable and stretchable electronic devices. However, the development of deformable energy generators that can attain extreme stretchability with superior healability, and transparency simultaneously is difficult to achieve due to the use of metallic electrodes. We address this issue by the use of an ionic conductor as the current collector in a triboelectric nanogenerator, resulting in a highly transparent, stretchable and self-healing device. The energy harvesting performance of ionic triboelectric nanogenerator is 12 times higher than that of the metallic based triboelectric nanogenerator due to the formation of an electrical double layer (EDL). The developed slime-based ionic conductor owing to the non-Newtonian behaviour of the current collector, an extreme stretchability as high as 700% was achieved without degrading the device performance, thus enables the triboelectric device to act as an a power source for highly deformable electronics. The device has a transparency of 92% transmittance, while transparency helps in the visual transmission of information, which can be potentially utilized in user-interactive displays, biomedical imaging, therapeutic optogenetics, and touch screens. Due to the weak hydrogen bonding interactions of the ionic conductor, the TENG can autonomously self-heal and can recover its performance even after 300 times of complete bifurcation. The resulting device demonstrates an extremely stretchable, highly transparent self-heal power source to be used as a power supplies for sensors, wearable electronics and soft robotics.

Triboelectric charging is an electrical charging phenomenon that occurs when different materials come into contact and separate spontaneously. Irrespective of the magnitude, all materials could be charged by contact. Some of the common materials consistently exhibit triboelectric charging patterns, and based on the charging characteristics, empirical “triboelectric series between materials” was constructed by arranging them according to the relative polarity of the contact charge acquired.

Recently, a triboelectric nanogenerator, which offers a unique solution to convert mechanical energy into electricity via combining the concept of triboelectric charging and electrostatic induction, was invented as a new technology of energy harvesting. Furthermore, using a similar principle, triboelectric sensors and tribotronics that utilize triboelectric output to drive and control electronic devices were also introduced. One of the important factors that determine the performance of the device is the material. However, materials known to exhibit triboelectric charging behavior are only limited to some polymers and a few metals already located in the triboelectric series. Further investigating the triboelectric charging behaviors of new materials and widening the material library of the triboelectric series are required.

Here, we investigated the triboelectric charging behaviors of various two-dimensional (2D) materials (MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, graphene, and graphene oxide), which have received great attention for decades owing to their distinct electronic, optical, mechanical, and thermal properties. The triboelectric charging behaviors were investigated using the concept of the triboelectric nanogenerator. Consistent results of contact-charging polarities were observed, using which, a modified triboelectric series including 2D materials was developed. For further verification, the effective work functions of the 2D materials, which are one of the main factors deciding their triboelectric charging behaviors, were estimated via Kelvin-probe force microscopy and calculated via first principles simulations as well. The charging polarity indicated the similar behavior regardless of the synthetic method and film thickness ranging from a few hundred nanometers (for chemically exfoliated and restacked films) to a few nanometers (for chemical-vapor-deposited films).

Further, the triboelectric charging characteristics could be successfully modified via chemical doping. This study provides new insights to utilize 2D materials in triboelectric devices, allowing the thin and flexible device fabrication.
We have performed an extensive high-throughput screening of known inorganic materials, in order to identify those that could be exfoliated into novel two-dimensional monolayers and multilayers [1]. The screening protocol first identifies bulk materials that appear layered according to a simple and robust chemical definition of bonding, determining then for all of these the binding energies of the respective monolayers, and their electronic state (metallic vs insulating), magnetic configuration (ferro-, ferrimagnetic, antiferromagnetic), and phonon dispersions (to evaluate mechanically stability). Such protocol identifies a portfolio of close to 2,000 inorganic materials that appear either easily or potentially exfoliable, to be investigated further for promising properties. First focus has been on the determination of the effective masses and mobilities (from the full solution of the Boltzmann transport equation) for electronic applications; of topological invariants; of superconductivity and charge-density waves; and of photocatalytic parameters for water splitting. Thanks to the use of the AiiDA (http://aiida.net) materials’ informatics platform, all the high-throughput calculations can be performed and streamed in fully searchable and reproducible ways, they are stored in a database with their full provenance tree of all parent and children calculations, and can be shared with the community at will.
large in the form of raw or curated data via the Materials Cloud (http://www.materialscloud.org) dissemination portal.


SESSION QN01.03: Data-Driven 2D Materials Discovery II
Session Chairs: Xiaofeng Qian and Meng Ye
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 128 A

1:30 PM *QN01.03.01
A Guided Safari Through the Properties of Over 1000 2D Materials Revealed by Data Mining Techniques Evan Reed; Stanford University, Stanford, California, United States.

Two-dimensional materials and weakly bonded layered materials exhibit potentially advantageous properties as thin electronic materials, but research has been largely focused on only a couple of dozen types. We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. I will provide a guided tour of the spectrum of properties of these materials that are of interest for electronic applications. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e., bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice.

2:00 PM QN01.03.02
A Simulation-Driven Database of 2D Materials for Growth Chambers Design Kasra Momeni1, Yanzhou Ji1, Kehao Zhang2, Joshua Robinson2 and Long-Qing Chen1; 1Louisiana Tech University, Ruston, Louisiana, United States; 2The Pennsylvania State University, State College, Pennsylvania, United States.

Chemical vapor deposition (CVD) is a powerful technique for synthesizing monolayer materials such as transition metal dichalcogenides. It has advantages over exfoliation techniques, including higher purity and the ability to control the chemistry of the products. However, controllable and reproducible synthesis of 2D materials using CVD is a challenge because of the complex growth process and its sensitivity to subtle changes in growth conditions, making it difficult to extend conclusions obtained in one CVD chamber to another. Here, we developed a multiscale model linking CVD control parameters to the morphology, size, and distribution of synthesized 2D materials, which then used for creating a database of growth condition-morphology relation. Its capabilities are experimentally validated via the systematic growth of MoS2. In particular, we coupled the reactor-scale governing heat and mass transport equations with the mesoscale phase-field equations for the growth morphology considering the variation of edge energies with the precursor concentration within the growth chamber. The predicted spatial distributions of 2D materials are statistically analyzed, and experiments are then performed to validate the predicted island morphology and distributions. It is shown that the model can be employed to predict and control the morphology and characteristics of synthesized 2D materials.

2:15 PM QN01.03.03
Rational Prediction of Synthesis of MAX Phases and MXenes Using Positive and Unlabeled Machine Learning Nathan Frey1, Jin Wang1, Gabriel Bellido1,2, Yury Gogotsi1,3 and Vivek B. Shenoy1; 1University of Pennsylvania, Philadelphia, Pennsylvania, United States; 2Office of Naval Research, Washington, Washington, United States; 3Drexel University, Philadelphia, Pennsylvania, United States.

Growing interest in the potential applications of two-dimensional (2D) materials has fueled advancement in the identification of new 2D systems with exotic properties. Increasingly, the bottleneck in this field is the synthesis of the materials. Although theoretical calculations have been able to predict a myriad of promising 2D materials, only a few dozen have been experimentally realized since the initial discovery of graphene. Here, we adapt the state-of-the-art positive and unlabeled (PU) machine learning framework to predict which theoretically proposed 2D materials have the highest likelihood of being successfully synthesized. Using elemental information and data from high-throughput density functional theory calculations, we apply the PU learning method to the MXene family of 2D transition metal carbides, carbonitrides and nitrides, and their layered precursor MAX phases, and identify 18 new MXene compounds that are highly promising candidates for synthesis. By considering both the MXenes and their precursors, we further propose 20 new synthetizable MAX phases that can be chemically exfoliated to produce new MXenes.

2:30 PM BREAK

SESSION QN01.04: Van der Waals Heterostructure
Session Chairs: Xiaofeng Qian and Meng Ye
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 128 A

3:00 PM *QN01.04.01
Localization with a Twist—Duality Between Configuration Space and Momentum Space in Incommensurate Stacked Layers of 2D Materials Efthimios Kaxiras and Stephen Carr; Department of Physics, Harvard University, Cambridge, Massachusetts, United States.

The stacking of individual layers of two-dimensional materials can be experimentally controlled with remarkable precision on the order of a tenth of a degree. The relative orientation of successive layers introduces variations in the electronic properties that can be controlled by the twist angle. We use simple theoretical models and accurate electronic structure calculations to predict that the electronic density in stacked 2D layers can vary in real space in a manner similar to the band-structure in momentum-space, creating moire super-lattices. A direct consequence of the patterns is the localization of electronic states. We demonstrate this effect in graphene, a semi-metal, and MoS2, a representative material of the transition metal dichalcogenide family of semiconductors. This effect can be useful in the design of localized electronic modes with specific geometries for experimental or technological applications, including superconductivity, as has been recently reported for 2D twisted bilayer graphene.

3:30 PM *QN01.04.02
Topics of Two-Dimensional Materials and Their Heterostructures Mei-Yin Chou1,2; 1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2School of Physics, Georgia Institute of Technology, Atlanta, Georgia, United States.

It has become possible in recent years to fabricate and manipulate two-dimensional nanomaterials in the laboratory that are as thin as one to few atomic layers. The reduced dimensionality gives rise to unique physical and chemical properties that differ from those of traditional bulk materials, and intriguing physical properties have been found in these few-layer systems. Computational studies have played a central role in understanding and predicting these novel properties. In this talk, I will focus on a few representative systems, including graphene systems and monolayers of transition metal dichalcogenides that exhibit properties ranging from charge density waves [1] to the quantum spin-Hall effect [2]. The hybrid system of boron nitride and graphene (h-BNC) at low BN doping serves as an ideal platform for band-gap engineering and valleytronic applications. The calculations find a linear dependence of the band gap on the BN concentration at low doping, arising from an induced effective on-site energy difference at the two C sublattices as
they are substituted by B and N dopants alternately. In addition, our calculations show that the Moiré patterns in van der Waals heterostructures will modify the local band gap, interlayer interaction, and structural parameters [3-5]. I will also discuss one-dimensional topological insulators manifested in graphene nanoribbons, in which localized spin states may exist at the end or near the junctions. A symmetry protected topological classification is formulated for any type of termination with quantized Berry phase when summed over all occupied bands.

References.

4:00 PM QN01.04.03
Plasmonic MXene Thin Films for Flexible Visible-Light Photodetectors

Dhinesh B. Velusamy, Jehad K. El-Demellawi and Husam N. Alshareef; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

MXenes, two dimensional (2D) nanosheets of transition metal carbides, have garnered significant interest due to their intriguing physicochemical properties associated with the unique 2 dimensionally confined chemical structures. These new classes of 2D materials have already shown promising electrochemical energy storage characteristics in both supercapacitor and Li-ion battery anode applications and endowed fascinating prospects for a variety of emerging applications in electronics, optics, energy conversion and storage. Recently, MXenes exhibited impressive optical properties e.g., tunable broadband absorption and intense surface plasmon excitations, underlining their potential for photonic and plasmonic devices. However, theoretical and experimental investigations in this context remain sparse and mainly limited to the most studied Ti3C2Tx MXene. Herein, we demonstrate molybdenum carbide MXene (Mo2Ct3) photodetectors for broadband visible light photodetection. The Mo2Ct3 MXene thin films deposited on paper substrates exhibit broad photosresponse in the range of 400-800 nm with high responsivity (9 A W⁻¹), detectivity (~5x10¹⁸ Jones) and reliable photo switching characteristics at a wavelength of 660 nm. Photodetectors made of four other MXenes have been also fabricated. We found that the photocurrent generation in Mo2Ct3 is principally controlled by surface plasmon-induced hot electrons. The existence and the distribution of a variety of surface plasmon modes over individual Mo2Ct3 nanosheets are visualized by the combination of scanning transmission electron microscopy (STEM) and ultra-high resolution electron energy loss spectroscopy (EELS). In addition, Mo2Ct3 thin film devices are shown to be resistant to environmental factors, illustrating their stable and durable photodetection operation. Moreover, the arrays of Mo2Ct3 thin film photodetectors are shown to be readily bendable under multiple and repeated deformations. The explicit ability to detect and excite individual surface plasmons, provide a viable platform for various MXene-based optoelectronic applications.

References.

4:15 PM QN01.04.04
2D Rules—Band Gap Engineering in Weakly Interacting van der Waals Heterostructures

Francis H. Davies, Ned T. Taylor, Shane G. Davies, Conor J. Price and Steven P. Hepplestone; Department of Physics and Astronomy, University of Exeter, Exeter, United Kingdom.

The band gap is of paramount importance to almost all of the electronic and optical properties of semiconducting materials. By controlling the size of the band gap and their electronic structure, we can control both the transport properties and the optical interactions of such materials. The ability to energetically control electrons in solid-state devices is pivotal in the fields of sensing, renewable energy [1], information processing and communications technology [2]. Here we present the rules of 2D band gap engineering in 2D heterostructures. Our insights offer the potential of engineering not just the band gap, but the electronic dispersion itself; making it far more versatile than strain engineering of band gaps.

The field of 2D semiconductors has been of growing research interest in recent years, but 2D heterostructures have only recently become experimentally viable [3]. We have performed a large scale first principles study of many transition metal dichalcogenides and other 2D semiconductors using density functional theory. These 2D layered heterostructures demonstrate weak inter-layer interactions. Due to this, the band structures of individual layers of a heterostructure have a high fidelity to their isolated counterparts. We show that a layered heterostructure will, therefore, have a dispersion which consists of an overlay of its components’ band structures. We determine that the electronic dispersions of 2D layered heterostructures can be tailored by layer composition, and demonstrate a wide range of potentially attainable tunable band structures.

1. Phys. Rev. B 92, 075439
2. Nat. Comm, 8, 15251
3. ACS Nano, 8, 9550

4:30 PM *QN01.04.05
Optical Properties of Two-Dimensional InSe, GaSe and Their Heterostructures, from Visible to the THz Range

Vladimir Falko; National Graphene Institute, University of Manchester, Manchester, United Kingdom.

We present the analysis of electronic band structure of InSe and GaSe films, from the stoichiometric mono- to N-layer films which determines optical properties of these 2D materials [1,2]. This study is based on the ab initio DFT and related multi-orbital tight-binding model analysis of the electronic band structure and wave functions in N-layer InSe and GaSe films, and it is compared to the results of ARPES and luminescence spectroscopy of this material [3]. We show [1,2] that the band gap in InSe (and GaSe) strongly depend on the number of layers, with a strong (more than two) reduction from the monolayer to crystals with N>6. We find that the conduction-band-edge electron mass in few-layer InSe is quite light (comparable to Si), which suggests opportunities for high-mobility devices and the development of nanocircuits. In contrast, the valence band in mono-, bi- and trilayer InSe is flat, opening possibilities for strongly correlated hole gases in p-doped films. Using the band structure and wave functions, we analyse optical transitions in thin films of InSe and GaSe, identify their polarisation and compare the results of modelling to the measurements performed on hBN-encapsulated atomically thin InSe and GaSe crystals.

Then, we show that the same materials have potential for optical functionality in the far-infrared range, for which one can exploit the intersubband transitions in InSe and GaSe few-layer films [4].

References.
Manipulating Light Flow with 2D Materials

The deliberate tailoring of semiconducting 2D transition metal chalcogenides for optoelectronic applications – via an understanding of their emergent electronic structure and photophysics in their chemical composition and atomic arrangement – presents significant opportunities, due to their strong light-matter interactions, reduced dimensionality, and chemical diversity and heterogeneity. Here, I will describe the use first-principles computational methods – including density functional theory, ab initio many-body perturbation theory, and materials databases – to predict and understand the electronic structure, chemical bonding, and excited state phenomena in these systems, leading to new intuitive and not important about class of materials. I will review our recent calculations of point defects, and in their impact on electronic structure and valley polarization, in 2D transition metal dichalcogenides; I will also discuss ongoing work in which we interface these systems with magnetic substrates to break valley degeneracy. Additionally, time permitting, I will discuss the opportunity for large nonlinear optical responses in monolayer transition metal monochalcogenides; and for photocatalytic reduction of CO₂. In each case, I will emphasize implications for experiments and new principles for the design of functional layer materials. This work supported by the Department of Energy and the Department of Defense; computational resources provided by NERSC.

9:00 AM QN01.05.02
Bright and Dark Exciton Landscape in Two-Dimensional Molybdenum Disulfide
Hongyu Yu¹; Magdalena Lauren¹ and Oleq Rubel²;¹ Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada; ²School of Physics, Nankai University, Tianjin, China.

Excitonic effects dominate the optical properties of materials, especially of low-dimensional materials such as transition metal dichalcogenides, e.g. monolayer molybdenum disulfide [1]. When considering the excitonic effect, the band structure changes remarkably which can even result in a change of the material’s bandgap type (e.g. from indirect to direct) [1]. However, while primary bright excitonic transitions are well studied, a systematic approach to dark transitions is still lacking. In this research, we study the excitonic effect in transition metal dichalcogenide monolayers starting with MoS₂ using density functional theory, quasiparticle methods (GW0) and the Bethe-Salpeter equation for calculating electronic excitations. In order to show the bandgap and exciton landscape, we include bright and momentum-resolved dark excitons in a novel approach of plotting the excitonic band structure. This way of visualizing the band structure allows us to easily tell if the material has a direct band gap after considering excitonic effects or not. Further, it enables the classification of dark excitons into spin-forbidden and/or momentum-forbidden transitions while clearly displaying the respective exciton binding energies. We believe that our approach will allow for exciting results, especially for the application to materials like ReSe₂ for which the nature of the band gap is still debated.


9:15 AM QN01.05.03
Tuning the Fröhlich Exciton-Phonon Scattering in Monolayer MoS₂
Bastian Müller¹, Jessica Lindlau¹, Andre Neumann¹, A.W. Holleitner¹, Alexander Högel¹ and Ursula Wurstbauer¹,²; Technical University of Munich, Garching, Germany; ²WWU Münster, Münster, Germany; ³LMU Munich, Munich, Germany.

A direct band gap [1], remarkable light-matter coupling [2] as well as strong spin-orbit and Coulomb interaction establish two-dimensional (2D) crystals of transition metal dichalcogenides (TMDs) as an emerging material class for fundamental studies as well as novel technological concepts. Valley selective optical excitation allows for optoelectronic applications based on the momentum of excitons [3]. In addition to lattice imperfections and disorder, scattering by phonons is a significant mechanism for valley depolarization and decoherence in TMDs at elevated temperatures preventing high-temperature valley polarization required for realistic applications [4]. Thus, a detailed knowledge about strength and nature of the interaction of excitons with phonons is vital. We directly access exciton-phonon coupling in charge tunable single layer MoS₂ devices by polarization resolved Raman spectroscopy. We observe a strong defect mediated coupling between the long-range oscillating electric field induced by the longitudinal optical (LO) phonon in the dipolar medium and the exciton. We find that this so-called Fröhlich exciton LO-phonon interaction [5] is suppressed by doping. This suppression correlates with a distinct increase of the degree of valley polarization of up to 60% even at elevated temperatures of 220 K [6]. Our result demonstrates a promising strategy to increase the degree of valley polarization towards room temperature valleytronic applications.

We acknowledge financial support by the DFG via excellence cluster “Nanosystems Initiative Munich” and DFG projects WU 637/4-1.


9:30 AM QN01.05.04
Manipulating Light Flow with 2D Materials Plasmons
Tony Low; Department of Electrical & Computer Engineering, University of Minnesota, Minneapolis, Minnesota, United States.

Recent years have observed a plethora of strong dipole type polaritonic excitations in 2D materials owing to the reduced screening. These polaritons can be sustained as electromagnetic modes at the interface between a positive and negative permittivity material. In the case of the plasmon-polaritons (e.g. in semi-metallic graphene), the negative permittivity is provided by the coherent oscillations of the free carriers. For exciton-polaritons (e.g. in semiconducting transition metal dichalcogenides, TMD) and phonon-polaritons (e.g. in diatomic hexagonal boron nitride, hBN), it is associated with their resonant optical absorption, resulting from a highly dispersive permittivity. These optical resonances can also result in a negative permittivity, albeit over a narrow spectral window.

In this talk, I will discuss our recent efforts in understanding plasmons behavior in 2D materials, such as graphene and its bilayer, black phosphorus, and transition metal dichalcogenides, and using them to control the flow of light both in the far- and near-field. The general constitutive materials response of 2D materials, in conjunction with metasurface approaches, can potentially enable arbitrary control of phase, amplitude, polarization and directionality of light.

10:00 AM BREAK

10:30 AM QN01.05.05
Photonic Response of 2D Nanostructures by Theoretical Analysis
Jie Jiang and Ruth Pechter; Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States.

Development of 2D transition metal dichalcogenides (TMDs) for photonic applications advanced greatly in recent years, for example, in providing improvements in optical nonlinearities, such as two-photon absorption (TPA) cross-sections. Interestingly, recently, even larger TPA cross-sections were measured for 2D organic-inorganic perovskites (OIPs). The 2D OIP structure emerges when Goldschmidt’s tolerance factor, which depends primarily on the ionic radius of the organic cation in this case, is larger than 1. 2D OIPs exhibit a large increase in the exciton binding energy due to quantum and dielectric confinement, and provide spectral tunability. Here we report on 2D OIPs with organic chromophore incorporation, in comparison to previously investigated cations, aiming to design materials for intensity enhancements. Density functional theory calculations of 2D OIP structures will be described, and quantification of the geometrical distortion by the bond length quadratic elongation, bond angle variance, and perovskite layer distortion. Electronic structure calculations, including spin-orbit coupling, demonstrate variations in the band alignments of the organic and inorganic parts, leading to varying confinement of the electrons and holes. The interplay between hybridization and band alignment type, as well as the calculated absorption spectra, as dependent on the chromophore type, will be discussed. Finally, in the context of tunability in the optical properties of 2D photonic nanostructures, the optical response of a defective monolayer TMD (WSe₂) will be reported.
Upon introduction of single or double Se vacancies, or a single V vacancy within monolayer WSe$_2$, the computational results demonstrate emergence of deeper defect excitons in comparison to shallower values observed for edges. Defect excitons are shown to red-shift significantly for large rotational defects that pattern the monolayer.

11:00 AM *QN01.05.06
Doped Graphene—Advantages for Sensing Individual Molecules 
**Mauricio Terrones**
The Pennsylvania State University, University Park, Pennsylvania, United States.

This talk will discuss the synthesis of large-area, high-quality monolayers of nitrogen-, silicon- and boron-doped graphene graphene sheets on Cu foils using ambient-pressure chemical vapor deposition (AP-CVD) [1-3]. Scanning tunneling microscopy (STM) and spectroscopy (STS) reveal that the defects in the doped graphene samples arrange in different geometrical configurations exhibiting different electronic and magnetic properties. Different substitutional nitrogen sites could be controlled by controlling the CVD temperature, flowrate and the duration of the doping precursor inside the reactor. Interestingly, these doped layers could be used as efficient molecular sensors. We will show that B-doped graphene (BG) exhibits unique sensing when detecting toxic gases such as NO$_2$ and NH$_3$. [2]. The detection limit for BG can reach as low as 95 ppt for NO$_2$ gas and 60 ppb for NH$_3$. BG has enhanced sensitivity values of 27 and 105 times better than graphene for NO$_2$ and NH$_3$ detection [3]. This is attributed to the presence of B atoms within the graphene lattice that results in a high affinity to both donor and acceptor molecules, leading to stronger interactions between the molecules and graphene. Finally we will discuss the use of graphene for enhancing Raman signals for specific molecules, also known as graphene enhanced Raman scattering (GERS). NG and Si-doped graphene (SiG) could significantly enhance the Raman signal of fluorescent molecules: Rhodamine B (RhB), crystal violet (CRV) and methylamine blue (MB) [1]. SiG exhibits an enhancement factor 10-40 times higher than that of PG (see Fig. 1) [1]. We will also show that by using NG as a substrate, Raman signals of dye molecules can be detected at a record low concentration of 10$^{-11}$ M [4]. This is very close to single molecular detection. However, this enhanced Raman sensing requires the Fermi energy of the substrate to match the LUMO level of the probe molecule, which allows an effective charge-transfer excitation [4].

References
Deep-level defects in wide-bandgap semiconductors exhibit localized electronic energy levels with paramagnetic spin states, and hence they constitute promising platforms for quantum bits (qubits). Defect-based solid-state spin qubits have been widely studied, including the nitrogen-vacancy (NV) center in diamond, vacancies in SiC, donor spins in silicon, and rare-earth ions, targeting quantum computing and sensing applications. The spin coherence time $T_2$, usually measured by Hahn-echo experiments, is a critical property for qubit applications. In quantum computers, in order to achieve quantum error correction, at least $10^9$ quantum gate operations need to be performed within $T_2$, yielding a desired coherence time larger than 100 $\mu$s. The sensitivity of quantum sensors, which is inversely proportional to $T_2$, benefits as well from qubits with long coherence times.

The decoherence of spin qubits can arise from different sources, including the magnetic noise from high-density paramagnetic defects and dangling bonds on the material surface. In highly purified bulk solids, the phase decoherence is mainly caused by the entanglement between the electron spin qubit and the nuclear spin bath of the host material. Thus, reducing the concentration of nuclear spins, e.g. through isotopic purification, is an effective technique to enhance $T_2$. For example, the ensemble $T_2$ of the NV center in diamond has been extended from 0.63 ms to 1.8 ms by reducing the concentration of $^{14}$C nuclear spins from 1.1% to 0.3%.

The nuclear spin density can also be reduced by decreasing the dimensionality of the nuclear spin bath from three dimension to two dimension or even lower dimensions. In addition, two-dimensional (2D) layered materials exhibit a variety of promising properties for the realization of hosts of defect-based spin qubits. 2D layered materials can be easily transferred and integrated into hybrid quantum systems. In 2D systems, point defects can be created and precisely located using a scanning transmission electron microscope or an annular dark field microscopy. Furthermore, compared with thin films of three-dimensional (3D) solids, 2D layers are free from unsaturated dangling bonds at the surface that are detrimental to spin coherence. However, the nuclear spin environments in many 2D materials are much more complex than, e.g. in diamond. Currently, h-BN and MoS$_2$ are among the most studied 2D material host candidates, and in h-BN all nuclei have large nuclear-spin moments.

In this talk, we investigate the coherence of spin qubits in 2D materials. We first explore the effect of dimensionality on spin decoherence and discuss the interplay of dimensionality, crystal geometry and nuclear spin concentration in determining $T_2$. We then predict the coherence time of spin qubits in 2D materials such as MoS$_2$ and h-BN, and show that isotopic purification can be much more effective in 2D than in 3D, leading to a spin coherence time of more than 30 ms in isotopically pure monolayer MoS$_2$. However achieving low nuclear spin concentration is not the only design rule to obtain optimal spin qubit hosts: the important roles of gyromagnetic ratios, homo-nuclear distance and nuclear magnetic moments are also discussed. Overall we predict that single-layer MoS$_2$ layers and delta-doped diamond slabs can be promising hosts for spin qubits, while the $T_2$ of h-BN appears to be much more challenging to engineer, due to the large gyromagnetic ratio of the boron nuclei.

This work is supported by NSF-MRSEC.

2:30 PM BREAK

3:30 PM *QN01.07.04
Origin of Antiferromagnetism and Magnetoelastic Effect in CrI$_3$ Bilayers Di Xiao; Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Since the demonstration of intrinsic ferromagnetism in atomically thin crystals, there has been a lot of interest in two-dimensional (2D) magnets. Among them, CrI$_3$ presents an intriguing case. While bulk CrI$_3$ is a ferromagnet, it becomes a layered antiferromagnet when thinned down to a few atomic layers. A number of interesting phenomena associated with this layered antiferromagnetism have been observed, including giant tunneling magnetoresistance and electrostatic doping control of magnetism. In this talk, I will present our study of the stacking dependent magnetism of bilayer CrI$_3$, using first-principles calculations. We show that the stacking order defines the magnetic ground state. By changing the interlayer stacking order one can tune the interlayer exchange interaction between antiferromagnetic and ferromagnetic. We propose that the predicted stacking-dependent magnetism can be probed via linear magnetoelastic effect. Our results not only gives a possible explanation for the observed antiferromagnetism in bilayer CrI$_3$, but also have direct implications in heterostructures made of two-dimensional magnets.

4:00 PM *QN01.07.05
Calculating Critical Temperatures for Ferromagnetic Order in 2D Materials—The Critical Role of Magnetic Anisotropy Daniele Torelli and Thomas Olesen; Technical University of Denmark, Roskilde, Denmark.

Magnetic order in two-dimensional (2D) materials is intimately coupled to magnetic anisotropy (MA) since the Mermin-Wagner theorem implies that rotational symmetry cannot be spontaneously broken at finite temperatures in 2D. Large MA thus comprises a key ingredient in the search for magnetic 2D materials that retain the magnetic order above room temperature. Magnetic interactions are typically modeled in terms of Heisenberg models and the temperature dependence on magnetic properties can be obtained with the Random Phase Approximation (RPA), which treats magnon interactions at the mean-field level. In the present work we show that large MA gives rise to strong magnon-magnon interactions that leads to a drastic failure of the RPA. We then demonstrate that classical Monte Carlo (MC) simulations correctly describe the critical temperatures in the large MA limit and agree with RPA when the MA becomes small. A fit of the MC results leads to a simple expression for the critical temperatures as a function of MA and exchange coupling constants, which significantly simplifies the theoretical search for new 2D magnetic materials with high critical temperatures. The expression is tested on a monolayer of CrI$_3$, which were recently observed to exhibit ferromagnetic order below 45 K and we find excellent agreement with the experimental value.

We apply the developed methodology to perform a computational screening for magnetic 2D materials with large critical temperatures based on the computational 2D database C2DB. We identify several stable materials, which are predicted to exhibit magnetic order above room temperature.

**SESSION QN01.08/QN02.07:** Keynote: Joint Session: Defects and Substrate Screening on the Electronic, Optical and Plasmonic Properties of 2D Materials

Session Chair: Oleg Yazyev

Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 129 A

4:30 PM *QN01.08.01/QN01.02.07.01
Defects and Substrate Screening on the Electronic, Optical and Plasmonic Properties of 2D Materials Steven Louie1,2; University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Symmetry, interaction and topological effects greatly influence the quantum properties of atomically thin two-dimensional (2D) materials. Defects and environmental screening can play equally important roles in determining their behaviors. In this talk I present several interesting phenomena related to point defects and substrate screening on the properties of 2D materials. 1) We study, using ab initio GW-BSE theory, the effect of point-defect chalcogen vacancies on the optical properties of monolayer transition metal dichalcogenides (TMDs). The chalcogen vacancies introduce unoccupied in-gap states and occupied resonant quasiparticle defect states. These defect states give rise to strongly bound defect excitons and hybridize with excitons of the pristine system, reducing the valley-selective circular dichroism. The results suggest a pathway to tune spin-valley polarization and other optical properties through defect engineering. 2) A fascinating property of monolayer semiconductors is that the electronic bandgap ceases to be an intrinsic physical parameter and can be engineered through the surrounding dielectric environment. We have exploited such a dielectric-dependent electronic bandgap and demonstrated the formation of a lateral heterojunction within a homogeneous MoS$_2$ monolayer through substrate engineering. The capability to tailor the local band structure and electrical transport in 2D semiconductors through dielectric engineering can open exciting new ways to design 2D nanoelectronic and optoelectronic devices. 3) Plasmons in atomically thin 2D materials are distinct from those of the bulk and traditional 2D electron gas systems. We have discovered that the plasmon dispersion in real quasi-2D metals is qualitatively different, being virtually dispersionless for wavevectors of typical experimental interest. This stems from a lack of continuous translational symmetry, making dispersionless plasmons a universal phenomenon in quasi-2D metals. Moreover, our ab initio calculations show that plasmons on monolayer metallic TMDs are long lived and localizable in wave packets (within ~15 nm) which does not significantly disperse over practical measurement time. Their slow propagation opens the possibilities of tracking plasmon wave packets in real...
time and of localizing long-lived, boson-like excitations in extended, atomically thin materials.

This work was supported by the U. S. Department of Energy, National Science Foundation, and Office of Naval Research. I would like to acknowledge collaborations with members of the Louie group.

SESSION QN01.09: Poster Session: 2D Layered Materials Beyond Graphene—Theory, Discovery and Design
Session Chairs: Xiaofeng Qian and Qinmin Yan
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

QN01.09.01
Two-Dimensional Cross-Linked Polythiophene Network 
Kongyang Yi and Dacheng Wei; State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai, China.

Solution-processed polythiophene thin films suffer from low efficient inter-molecular carrier hopping and undermined conjugation arising from chain twist and random entanglement. To form a graphene like two-dimensional (2D) cross-linked conjugated polymer network is one of promising strategies to solve this problem. Here, we synthesize decimeter-sized 2D cross-linked polythiophene network (2DPT) by surface-confined Ullmann coupling, with 1.6 nm thickness and transmittance of ~97% at 550 nm. The 2D cross-linked network improves charge carrier transport, resulting in carrier mobility up to 4.6 cm² V⁻¹ s⁻¹ and conductance of 206 S cm⁻¹, much higher than that of normal solution-processed conjugated polymer films. Owing to efficient carrier transport, atomic thickness and large conjugated surface, this new conjugated polymer exhibits fast response to stimuli as the channel in a liquid-gated H₂SO₃ sensor, and low contact resistance as bottom-contact electrodes in organic field effect transistors with high carrier mobility.

QN01.09.02
A Nonthermal Plasma Synthesis Route to Two-Dimensional MoS₂
Chad Beaudette, Jacob Held, Andre Mkhiyan and Uwe Kortshagen; University of Minnesota, Minneapolis, Minnesota, United States.

In this work we investigate the production of two-dimensional molybdenum disulfide, MoS₂, through two nonthermal based routes of synthesis: plasma enhanced atomic layer deposition (PEALD) and plasma enhanced chemical vapor deposition (PECVD). MoS₂ is a class of van der Waals two-dimensional materials whose applications include transistors, memristors, hydrogen evolution reactions, photodetectors, lithium ion batteries, water purification, and dye sensitized solar cells. However, many production methods for two-dimensional molybdenum disulfide suffer from either high temperatures, long time scales, dangerous chemicals (hydrogen sulfide) or low yield. Here, we describe two processes capable of producing large area films of MoS₂ utilizing molybdenum pentachloride and elemental sulfur as precursors. Both PECVD and PEALD can produce polycrystalline material at low temperatures (275-315 °C). In the case of PECD grown films, time scales for nucleation and large area growth occurs on the order of one to two minutes to produce few layer molybdenum disulfide. For PEALD, due to the steric factor of the molybdenum pentachloride precursor, only 2 cycles are required for a complete polycrystalline two-layer MoS₂ film with Angstrom level surface roughness. Film quality and structure are confirmed by Raman spectroscopy, transmission electron microscopy, and atomic force microscopy. This work was supported primarily by the U.S. National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program.

QN01.09.03
Etching Anions from Layered Materials for MXene-Like Synthesis of 2D Materials 
Daniel Druffel, Katie Scott, Jacob Pawlik and Scott Warren; Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

MXenes have attracted significant attention since their discovery because their elegant synthesis yields nearly 100% monolayer samples. MXenes are prepared from a layered MAX (metal aluminum carbide) phase by selectively etching layers of aluminum (or Si, Ga) atoms using HF, leaving the 2D metal carbide lattice intact. Building on the synthetic concepts of MXenes, here we report the first synthesis of 2D materials made by selectively etching halides from layered phases. First, we synthesized layered metal carbide iodides by high temperature reactions of the metal, carbon, and the metal iodide. By tuning the temperature, pressure, and stoichiometry, we produced powders consisting of thin platy crystals about 1 μm thick and 10-100 μm. Then we explored routes to etch the iodide layers selectively, including solution-based methods using lithium naphthalide as the etchant and a gas-phase method using potassium vapor at 200 °C. Like the oxidative etchings used to produce MXenes, we find that these reductive etchings produce materials with hollow, accordion-like behaviors, which can be delaminated further by sonication to few-layer 2D materials. We performed X-ray diffraction to reveal that the reaction of layered metal carbide iodides with potassium vapor extracts iodide and forms potassium iodide, which can be dissolved and removed. Interestingly, unlike traditional MXenes, the surface of the reductively etched metal carbides do not have hydroxyl or fluoride ions bound to the surface. In fact, our XAFS calculations show that the reductively etched 2D materials, under appropriate conditions, can remain functionalized at the surface, offering unique properties that could be useful in a number of applications in energy storage, catalysis, and electronics. Motivated by our initial promising findings, further experimental characterization of the 2D materials and their surfaces are underway.

QN01.09.04
Highly Crystalline Synthesis of vdW Tellurene Sheets on Two-Dimensional Surfaces 
Sijie Yang, Bin Chen, Ying Qin, Yi Zhou, Lei Liu, Michael Darso, Houlong Zhuang, Yuxia Shen and Sefaattin Tongay; Arizona State University, Tempe, Arizona, United States.

Recent results have identified two-dimensional (2D) tellurene as a potential van der Waals (vdW) material for thermoelectric and optoelectronics applications owing to their pseudo-one-dimensional (anisotropic) behavior and structure. While hydrothermal synthesis is suitable for yielding potentially crystalline materials, it is well known for its incompatibility with manufacturing and scaling. This talk will introduce novel synthesis of tellurene sheets onto a variety of surfaces of vdW-bonded 2D layered crystals. Our systematic tellurene growth studies on six different vdW surfaces show that GaSe and GaS surfaces enable highly crystalline and self-oriented tellurene sheets. Detailed cross-sectional transmission electron microscopy (TEM), angle-resolved Raman spectroscopy, scanning electron microscopy, and energy-dispersive spectroscopy measurements provide fundamental insights into the growth dynamics and characteristics of tellurene. First-principles calculations and cross-sectional TEM measurements suggest that tellurene chains are well-oriented along the GaSe armchair lattice direction owing to the much-reduced total energy of the system and a stronger degree of coupling across adjacent layers. Synthesized tellurene sheets exhibit remarkable structural anisotropy, as evidenced by angle-resolved Raman measurements, and the overall results open a clear pathway for layer-by-layer growth of tellurene sheets with controlled crystalline anisotropy through conventional synthesis techniques.

QN01.09.05
High-Throughput Prediction and Charge-Transfer Stabilization of Multidimensional Electrides 
Jack D. Sundberg, Daniel Druffel, Jacob Pawlik, Adam Woonger and Scott Warren; University of North Carolina, Chapel Hill, North Carolina, United States.

Electrides have gained considerable attention in recent literature thanks to demonstrated applications as superconductors, catalysts, and solid-state dopants. However, current electrode materials are largely limited by the tradeoff between desired electronic properties and the preventive reactivity of these materials. This is caused by the distinctive feature of electrodes: bare-electrons that exist at isolated lattice sites. Further, reactivity increases when bare electrons form interconnected pathways, but these ‘multidimensional’ electrides also provide desirable properties like heightened electrical conductivity. Thus, this tradeoff must be addressed by discovery of electrides specialized for given applications (i.e. where stability is vital) and/or stabilization of highly desired multidimensional electrides. Both strategies are employed here. High-throughput screening is used to address the scarcity of stable multidimensional electrides and propose a new series of robust, low-work function compounds. This screening is driven by derivatives of known halide materials, where electrochemical dehalogenation can produce electrode forms, and the synthetic approach is experimentally demonstrated with previously reported two-dimensional (layered) electrides. By avoiding high-temperature synthesis, kinetically stable and oxidation-resistant electrodes can be realized. Secondly, stabilization of known and
newly reported electrodes are computationally examined and experimentally applied via novel charge-transfer stabilization at the electrode-substrate interface. By reducing the reactivity of electrodes, previously metastable forms can be synthesized as electrode thin-films, where their increased surface area is idealistic for the aforementioned applications and further enables new uses. Together, the discovery of multidimensional electrodes and charge-transfer stabilization expands on reported multidimensional electrodes and their corresponding applications as low work-function materials.

QN01.09.06
Large-Area Ultra-Clean Dry Transfer of 2D Materials by Spin-Coated Pressure Sensitive Adhesive Polymers Yoon Seok Choi, Dong Heon Shin and Byung Hee Hong; Seoul National University, Seoul, Korea (the Republic of).

In recent years, researchers have tried to develop various methods to synthesize high-quality large-scale graphene using chemical vapor deposition (CVD) processes. However, the performance of CVD graphene is often degraded by defects, cracks and polymer residues that occur during transfer processes, which causes the similar problems in the transfer of other 2D materials. The PMMA coating is still a very effective method for the transfer of 2D materials, but the wet process to remove PMMA using acetone is problematic for device integration with soluble layers. Here we report a novel transfer method based on the use of pressure sensitive adhesive (PSA) that can be simply spin-coated on the sample, and completely removed by peeling-off after transfer, which is expected to allow the use of soluble layers for various 2D device fabrication processes. We confirmed that the sheet resistance of graphene has not been altered after transfer thanks to the good adhesion between graphene and PSA layers. In addition, the transparent graphene FETs transferred by PSA shows high charge carrier mobility compared to the FETs transferred by PMMA or thermal release tapes (TRT), implying that the graphene surface is ultra-clean without residues after the removal of PSA. We believe that the current method is applicable to various flexible and wearable applications that have been limited by wet transfer conditions for more practical and larger scale device fabrications of 2D materials.

QN01.09.07

Two-dimensional (2D) materials can be single layer because the bonds between each layer are made up of Van der Waals bonds while interlayer atoms bind together as covalent bonds. They can be separated into atomic-level single layers, which are very flexible and transparent, and are suitable for future electronics because of their various electrical and physical properties. Among 2D materials, MoS2 has drawn much attraction and chemical vapor deposition (CVD) is most popular method for synthesizing large size 2D materials. However, this process is difficult to control the temperature accurately and causes problems of the non-uniformity depending on the distance (sulfur position), and the internal contamination of furnace. In this study, a novel chemical vapor deposition (CVD)-free and solution-processed synthetic method were developed and successfully synthesized large size and uniform MoS2 thin films. The MoS2 precursor solution was formulated by sulfur-dissolving method to obtain uniform coating property. MoS2 thin films were prepared by simple spin-coating and one-step annealing method without any CVD process (CVD-free). The solution-synthesized MoS2 thin films were characterized to confirm 2H-MoS2 structure. The various atomic layers of synthesized MoS2 could be controlled with the precursor concentrations, such as two-layer for 0.0070 M, three-layer for 0.0125 M, and five-layer for 0.025 M of MoS2 precursor solution, which were confirmed by STEM.

QN01.09.08
Size and Strain Effects on Mechanical and Electronic Properties of 2D Green Phosphorene Monolayer and Nanoribbons Guang Yang1, 2; Evan Garrison1; Tianxing Ma3 and Xihong Peng1; 1Arizona State University, Mesa, Arizona, United States; 2Beijing Normal University, Beijing, China.

A phosphorus isomer named green phosphorus was recently predicted by theory with a similar interlayer interaction compared to that of black phosphorus, which indicates that individual layers can be mechanically exfoliated to form two-dimensional (2D) layers called green phosphorene. This 2D monolayer showed high stability and was predicted to have a direct band gap up to 2.4 eV. First-principles density functional theory calculations were used to investigate the mechanical properties and strain effect on electronic band structure of the 2D green phosphorene along two perpendicular in-plane directions, namely armchair and zigzag. It was found that the 2D green phosphorene ribbon with width up to 57 Å. Effects of ribbon width (size) and strain on the mechanical and electronic properties of the ribbons were studied. The Young’s modulus, effect of quantum confinement on the band gap, and effect of strain on the electronic band structures of the ribbons were investigated. The green phosphorene ribbons were found to exhibit prominent anisotropic properties, with the Young’s modulus in the range of 10-35 GPa for the armchair green phosphorene nanoribbons (AGPNR) and 160-170 GPa for the zigzag green phosphorene nanoribbons (ZGPNR), which are the same order of magnitude as those of its 2D sheet. The work function was found to be between 5 eV – 5.7 eV for the range of ribbon widths studied. Both size and strain trigger direct-indirect bandgap transition in the ribbons and their transition mechanisms were discussed.

QN01.09.09
Investigating the Exfoliation of Ni-B 2D Sheets from Ni2ZnB MAB Phase Amir Rezaei and Boniface Fokwa; University of California, Riverside, Riverside, California, United States.

MXene materials, 2D transitional metal carbides, have shown some promising properties in battery, supercapacitor and energy applications. These 2D layers have been exfoliated from ternary carbides named MAX phases. However, recently, a new group of 2D materials called MBene have been in interest since they have a similar structure and exfoliation mechanism to MXene. In this study, we discuss the possibility of forming 2D Nickel boride layers via selectively etching Ni2ZnB MAB phase. Single phase Ni2ZnB MAB phase has been synthesized for the first time. The zinc interlayer was then etched out, via immersing the MAB phase in diluted HCl. The selectively etched particles were investigated via scanning electron microscopy and powder X-ray diffraction. It was observed for the first time that ternary Ni2ZnB phase can be exfoliated via selectively etching the zinc interlayer. Demonstrating the zinc interlayer etching opens a door to the synthesis of a large number of new 2D borides from ternary MAB phases, especially those containing Zn.

QN01.09.10
Intercalation-Tuned Chemochromism in 2D Layered MoO3 Bryan P. Moser and Kristie Koski; University of California, Davis, Davis, California, United States.

We demonstrate that intercalation of zero-valent atoms can be used to chemically change the color of molybdenum trioxide (MoO3) from transparent white to dark blue. Chemochromism is achieved through dilute creation of a zero-valent atomic species in solution (such as V, Mo, Sn, and Co) which is then intercalated into the van der Waals gap. Chemochromism of MoO3 is shown to be reversible, robust, and has remarkably high absorptivity. We show that this 2D layered oxide shows promise in color-changing smart devices.

QN01.09.11
Linking DFT Calculations on Hydroxyl Group Concentration with Experimental ALD Growth Mechanics Matthew Lawson; Materials Science and Engineering, Boise State University, Boise, Idaho, United States.

Transition metal dichalcogenides (TMDs) are rapidly becoming of interest when transitioning from bulk phase to two dimensional structures. Not only do they boast high carrier mobilities, but first-principles calculations and experimental results have demonstrated that methods like doping and alloying can tailor critical properties such as the band gap. Now, the focus on first-principles calculations on TMDs has shifted from predicting performance and properties, to understanding and controlling TMD growth and processing. Our experimental collaborators have successfully growth MoS2 via atomic layer deposition (ALD) but have little insight into how the hydroxyl concentration on the substrate affects growth kinetics. We use density functional theory (DFT) to model the initial growth mechanisms between the gas precursors and substrate and predict the optical hydroxyl surface concentration for ALD growth. By thermally controlling hydroxyl groups on our alumina surface we characterize our substrates with x-ray photoelectron spectroscopy (XPS) to determine experimental hydroxyl concentration. We propose a novel approach of combining DFT calculations and ALD growth measurements for finding optimal
CO\textsubscript{2} Capture and Conversion Chemistry with 2D Layered Materials

Calley N. Eads, Samuel A. Tenney, Ashley R. Head and Dario Stacchiola; Brookhaven National Laboratory, Upton, New York, United States.

CO\textsubscript{2} emissions have increased substantially in recent years, to a point that is detrimental to the environment and needs to be addressed. Methods to capture CO\textsubscript{2} and convert the greenhouse gas into its fundamental components are underway but are currently energy-intensive. We aim to approach this existing problem with novel materials, such as doped-2D layered materials and metal-organic frameworks on metal supports, and understand the interfacial interactions using microscopy, infrared and photoemission spectroscopy at near-ambient pressures.

Mechanical and Thermal Properties of Grain Boundary in a Planar Heterostructure of Graphene and Hexagonal Boron Nitride

Anran Wei and Yinfeng Li; Department of Engineering Mechanics, Shanghai Jiao Tong University, Shanghai, China.

In this study, the mechanical properties of grain boundaries (GBs) in planar heterostructures of graphene and hexagonal boron nitride (h-BN) were studied using the molecular dynamics method in combination with the density functional theory and classical disclination theory. The hybrid interface between graphene and h-BN grains was optimally matched by a non-bisector GB composed of pentagon-heptagon defects arranged in a periodic manner. GB was found to be a vulnerable spot to initiate failure under uniaxial tension; moreover, the tensile strength was found to anomalously increase with an increase in the mismatch angle between graphene and h-BN grains, i.e., the density of pentagon-heptagon defects along the GBs. The disclination theory was successfully adopted to predict the stress field caused by lattice mismatch at the GB. Comparison between stress contours of GBs with different mismatch angles demonstrates that the arrangement of 5\textendash{}7 disclinations along the GB is crucial to the strength, and the stress concentration at the GB decreases with an increase in disclination density; this results in an anomalous increase of strength with an increase in the mismatch angle of grains. Moreover, the thermal transfer efficiency of the hybrid GB was revealed to be dependent not only on the mismatch angle of grains but also on the direction of the thermal flux. Thermal transfer efficiency from graphene to h-BN is higher than that from h-BN to graphene. Detailed analyses for the phonon density of states (PDOS) of GB atoms were carried out for the mismatch angle-dependence of interfacial conductance. Our results provide useful insights for the application of two-dimensional polyhexystalline heterostructures in next-generation electronic nanodevices.

Growth of MoS\textsubscript{2} Nanotubes by Chemical Vapor Deposition Using FeO Nanoparticles as Catalysts

Takashi Yanase, Mengting Weng, Fumiya Uehara, Taro Nagahama and Toshihiro Shimada; Engineering, Hokkaido University, Sapporo, Japan.

Introduction: MoS\textsubscript{2} nanotube (MoS\textsubscript{2}NT) that composed of semiconducting layered material has potential applications to the sensors, transistors, catalysts, etc. due to the unique 1D geometry and the edge state. Several methods have been used to synthesize MoS\textsubscript{2}NT such as physical vapor transport, thermal decomposition of the precursor and hydrothermal synthesis. However, there were some disadvantages in these methods, for example, long time reaction and necessity of toxic gas (H\textsubscript{2}S). Therefore, it is important to establish the economical and environmentally friendly way for the synthesis. We found that MoS\textsubscript{2}NT can be synthesized by chemical vapor deposition (CVD) using SiO\textsubscript{2}/Si substrate dispersed with FeO nanoparticles\textsuperscript{(1\textendash{}3)}. It can be considered that FeO nanoparticles work as catalysts as seen in the growth of carbon NT. The characterization and the growth mechanism of the MoS\textsubscript{2}NT are focused in this study.

Method: MoS\textsubscript{2}NTs were synthesized using a home-built CVD apparatus\textsuperscript{(3)} with two-flow system. Several kinds of metal or metal oxide nanoparticles (Fe, FeO, Fe\textsubscript{2}O\textsubscript{3}, CuO, Cu\textsubscript{2}O, NiO) were used to investigate their catalytic activity. SiO\textsubscript{2}/Si wafers dispersed with the nanoparticles were used as substrates. The temperatures and flow rates of the source materials (MoO\textsubscript{3} and sulfur) were separately optimized for the growth of the MoS\textsubscript{2}NTs. The MoS\textsubscript{2}NTs were characterized by transmission electron microscopy, energy dispersive spectrometry and Raman spectroscopy.

Results and Discussion: Among the prepared nanoparticles, only FeO is active for the synthesis of MoS\textsubscript{2}NT. Nothing or leaf-shape MoS\textsubscript{2} formed when the other nanoparticles were used. This is probably because FeO nanoparticles are reactive due to the O vacancy (non-stoichiometry) and Fe-Mo-S system forms layered material. We also found that the shape of the FeO nanoparticles affect the yield of the MoS\textsubscript{2}NTs. The spherical and truncated octahedral FeO nanoparticles can be synthesized by optimizing the synthetic conditions\textsuperscript{(4)}. It was found that the truncated octahedral FeO nanoparticles have greater catalytic activity than the spherical one. This is probably because the MoO\textsubscript{3} and sulfur vapor easily deposit on the sharp edges. Furthermore, the size of MoS\textsubscript{2}NTs also affects the growth of MoS\textsubscript{2}NT. SEM images clearly revealed that the 30-nm truncated octahedral FeO nanoparticles show the highest catalytic activity among the prepared FeO. The NTs on the SiO\textsubscript{2}/Si substrate were identified as MoS\textsubscript{2} by Raman spectroscopy because the two distinctive peaks, A\textsubscript{1g} and E\textsubscript{2g}, were detected. EDS spectra that showed the existence of Mo and S is another evidence for the formation of MoS\textsubscript{2}. The growth mechanism was concluded as VS mechanism by TEM observation because there was no FeO nanoparticles on the tip of the MoS\textsubscript{2}NT. The TEM observation also clarified that the MoS\textsubscript{2}NT has multilayer structure. The chirality of MoS\textsubscript{2}NT was armchair that was determined by electron diffraction pattern.

References


Hydrophilic Tannic Acid-Modified WS\textsubscript{2} Nanosheets for Enhanced Polysulfide Conversion in Aqueous Media

Yuheng Tian; University of New South Wales, Kensington, New South Wales, Australia.

Polysulfide-based organic battery systems have demonstrated great potential for large scale energy storage, but are restricted by the cost and the flammability of the organic solvents. It would be ideal to establish the aqueous-based polysulfide electrochemistry to enable cost-effective stationary energy storage. However, the sluggish reaction kinetics of polysulfide placed serious fundamental barrier to implementation. Here we developed hydrophilic tannic acid-modified WS\textsubscript{2} nanosheets as polysulfide conversion electrocatalysts in alkaline aqueous solutions. The tannic acid not only acted as a negatively charged surfactant to effectively delaminate the bulk WS\textsubscript{2} sheets, but also functionalized the delaminated WS\textsubscript{2} nanosheets through the coordination of tannic acid functional groups with tungsten atoms resulting in greatly improved hydrophilicity. Using graphene as the conductive support, the tannic acid-modified hydrophilic WS\textsubscript{2} nanosheets demonstrated a promoting electrocatalytic activity for polysulfide oxidation and reduction in aqueous solution. The incorporation of tannic acid imposed the collective interactions between polysulfide and the hydrophilic WS\textsubscript{2} nanosheets via the negatively charged molecules and the polar surfaces. With a 0.5 M Li\textsubscript{2}S\textsubscript{2} electrolyte, the graphene and modified WS\textsubscript{2} mixture gave an areal specific capacity of 0.37 mA h/cm\textsuperscript{2}, compared to 0.27 mA h/cm\textsuperscript{2} for the pure graphene.

2D Titanium Carbide (MXene)/Silver Nanoparticle Hybrid Material for Highly Sensitive and Selective Surface-Enhanced Raman Scattering

Abubakar Mohammed, Tej Limbu, Martha Garcia, Fei Yan, Bassant Chitara, Jacob Boggs, Lauren Odom and Yongan Tang; North Carolina Central University, Durham, North Carolina, United States.

Transition metal carbides (MXenes) have emerged as a promising family of 2D layered materials, and are considered as potential candidates for a myriad of applications including plasmonic sensing due to their outstanding electronic, optical, mechanical, and thermal properties. Herein, we report a flexible and reusable substrate made from a hybrid material consisting of 2D titanium carbide MXene (Ti2C) and silver nanoparticles, fabricated by spray coating for highly sensitive surface-enhanced Raman scattering (SERS). The 2D Ti2C layers were delaminated from their bulk Ti2C\textsubscript{10} MAX phase by using a mixture of hydrochloric acid and potassium fluoride as the etchant solution and silver nanoparticles were synthesized by thermal reduction of silver trifluoroacetate in soxymethyl ether in the presence of oleic acid. The as-prepared hybrid materials were characterized by UV-visible spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy, and X-ray diffractometry. The plasmonic properties of 2D Ti2C/silver nanoparticles hybrid material was evaluated with several organic dyes, which showed significantly different enhancement factors for different dyes.
In this talk, I present recent theoretical discoveries of several fascinating manifestations of topological effects in the electronic and optical properties of atomically thin one-dimensional (1D) and two-dimensional (2D) materials. First, we find that symmetry-protected topological phases exist in graphene nanoribbons (GNRs) [1]. Semiconducting GNRs of different width, edge shape, and terminating unit cells can belong to different electronic topological classes, characterized by a $Z_2$ invariant. Junctions between segments of topologically distinct GNRs are predicted to support robust in-gap topological junction states which can be used for band engineering. Experimental realizations of these predictions have been achieved [2]. Second, we show that the conventional optical selection rules for excitons must be replaced in 2D by a novel simpler formula, owing to a topological characteristic inherent to the photocexcitation of excitons in 2D [3]. The new selection rule is dictated by a winding number of the interband optical transition matrix elements (a heretofore unrecognized topological invariant). This appealingly simple and general new rule is applied to elucidate the optical spectra of gapped graphene systems [4]. Finally, if time permits, I will discuss some very recent work on the effects of electron-hole interactions on shift currents in non-centrosymmetric 2D crystals (the so-called bulk photovoltaic effect), in which we show excitonic effects lead to an enormous enhancement and, more interestingly, gives rise to DC conduction with sub-bandgap-frequency excitations [5].

This work was supported by the U. S. Department of Energy, National Science Foundation, and Office of Naval Research. I would like to acknowledge collaborations with members of the Louie group.

References:

9:00 AM QN01.10.02 Application of High-Throughput DFT Methods to Low-Dimensional, Topological and Energy-Related Materials Kamal Choudhary and Francesca Tavazza; MML, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

JARVIS (Joint Automated Repository for Various Integrated Simulations) is a NIST-developed, unique integrated framework to accelerate material design using classical force-fields (FF), density functional theory (DFT) and machine learning (ML). The JARVIS-DFT hosts data for more than 30000 bulk and 800 monolayer materials. We identified more than 1500 2D materials using lattice parameter criteria and carried out exfoliation energy calculations. We charted improved lattice parameters and formation energies using van der Waals functional for all the 30000 materials in the database and also calculated elastic tensors for more than 12000 bulk and 250 monolayer materials. Using the above data, we established relations between exfoliation energies and elastic constants. To alleviate bandgap underestimation in conventional DFT and to improve frequency dependent dielectric function predictions, we re-evaluated band gaps and dielectric functions using meta-GGA based approaches for more than 10000 materials. We used a spectroscopic limited maximum efficiency approach to identify potential photovoltaic materials. Using spin-orbit spillage criteria, we identified more than 1500 potential topological materials including topological insulators, Weyl and Dirac semimetals, and topological crystalline insulators. The database is publicly available at https://jars.nist.gov/.

9:15 AM QN01.10.03 Quantum Nonlinear Ferroic Optical Hall Effect Hua Wang and Xiaofeng Qian; Department of Materials Science and Engineering, Texas A&M University, College Station, Texas, United States.

Nonlinear optical responses provide basis for ultrafast probing of material's intrinsic symmetry. Here we present first-principles theory of quantum nonlinear ferroic optical Hall effect (QNFHE), a Hall like photocurrent originated from the second order current response in (multi-)ferroics. The interplay of crystalline, permutation, gauge, time reversal symmetries and inherent causality governs the symmetry of QNFHE. We elucidate QNFHE in a class of 2D multiferroics using first-principles calculations and group theoretical analysis. Our results suggest QNFHE-based optical technique as a route for ultrafast characterization of multiferroic order and domain evolution in multiferroic materials. These microscopic understandings of QNFHE from first-principles theory, together with very recent discoveries of 2D ferroics/multiferroics, will open up a variety of new avenues for nonlinear optoelectronics. This research was supported by the National Science Foundation under award number NSF DMR-1753054. References: [1] H Wang and X Qian, Nano Letters 17, 5027-5034 (2017). [2] H Wang and X Qian. 2D Materials 4, 015042 (2017). [3] H Wang and X Qian. Quantum Nonlinear Ferroic Optical Hall Effect, submitted (2018).

9:30 AM QN01.10.04 Optoelectronic Properties of Topological Transition Metal Chalcogenides Ji Feng; Peking University, Beijing, China.

Transition metal chalcogenides have traditionally attracted broad research attention owing to their unique layered structure and the coexistent charge-density wave, superconductivity and correlation effects, among other things. The reason for the recent surge of interest in this family of materials is two-fold: they are precursors to fascinating 2-dimensional materials, and some members are topological. In this talk, we will report our computational and theoretical progresses in the studies of topological insulating and metallic transition metal chalcogenides. In particular, we will discuss the interaction-induced quantum spin Hall gap in 17 $\text{WTe}_2$, where it is found that a positive band gap is present in the hybrid density functional approach. The nonlinear optical properties in type II Weyl semimetal TaI$_2$Te, will also be reported, where usually large photocurrents owing to the presence of Weyl nodes are detected by our collaborators. I will discuss how symmetry determines the nonlinear optical response in this material, in conjunction analysis with quantitative computation of effective third-order response functions.

10:00 AM BREAK

10:30 AM QN01.10.05 Topological Magneto-Optical Effect and Its Quantization in Noncoplanar Antiferromagnets Yugui Yao; School of Physics, Beijing Institute of Technology, Beijing, China.

Magneto-optical (MO) effects, referring to changes in the polarization state of light upon interacting with magnetic matter, are one of the most basic phenomena in solid-state physics. MO effects have been known for more than a century, whose origin is usually ascribed to the simultaneous presence of band exchange splitting and spin-orbit coupling. However, using a tight-binding model and first-principles calculations, we show that topological MO effects, in analogy to the topological Hall effect, can arise in noncoplanar antiferromagnets entirely due to the scalar spin chirality instead of spin-orbit coupling. Here, the band exchange splitting and spin-orbit coupling are not required for topological MO effects. Moreover, we discover that the Kerr and Faraday rotation angles in two-dimensional insulating noncoplanar antiferromagnets can be quantized in the low-frequency limit, implying the appearance of quantum topological MO effects, accessible by time-domain THz spectroscopy [1]. Also, I will show our group’s recent research results on MO effects in novel two-dimensional materials if time permits [2-5].
References:

11:00 AM *QN01.10.06
Prediction of 2D Topological Insulators from First-Principles Calculation Honming Weng; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Two-dimensional (2D) topological insulators (TIs) have been recognized as a new class of quantum state of matter. They are distinguished from normal 2D insulators with their nontrivial band-structure topology identified by the Z2 number as protected by time-reversal symmetry (TRS). 2D TIs have intriguing spin-velocity locked conducting edge states and insulating properties in the bulk. In the edge states, the electrons with opposite spins propagate in opposite directions and the backscattering is fully prohibited when the TRS is conserved. This leads to a quantized dissipationless “two-lane highway” for charge and spin transportation and promises potential applications. Up to now, only very few 2D systems have been discovered to possess this property. The lack of suitable material obstructs further study and application. In this talk, I will introduce by using first-principles calculations we have proposed that the layer compounds ZrTe5 and HfTe5, the transition metal dichalcogenide (TMD) haekelites with square-octagonal lattice, the functionalized MXenes with oxygen M2CO2 (M=W, Mo, and Cr), are 2D TIs with quite large band gap. Importantly, ZrTe5 and HfTe5 are very easily to be synthesized by exfoliating. This will pave the way to tremendous applications of 2D TIs, such as “ideal” conducting wire and the realization of topological superconductivity and Majorana modes for quantum computing.

References:
First-Principles Prediction of Stable Transition Metal Dichalcogenide Alloys

John Cavin 1, Sung B. Cho 2 and Rohan Mishra 2; 1Department of Physics, Washington University in St. Louis, St. Louis, Missouri, United States; 2Virtual Engineering Center, Korea Institute of Ceramic Engineering and Technology (KICET), Ichon, Korea (the Republic of); 1Department of Mechanical Engineering and Material Science, Washington University in St. Louis, St. Louis, Washington, United States.

Quasibinary alloying among pairs of 2-dimensional (2D) transition metal dichalcogenides (TMDs) is an attractive method for tuning properties for applications such as optoelectronics and catalysis. Of the many possible combinations of TMDs, the small subset of semiconductor alloys has garnered widespread attention. Outside this limited subset, the synthesizability of alloys remains largely unknown. In order to guide the synthesis of such alloys, we present ab initio calculations of equilibrium phase diagrams with regions of stability for 27 TMD alloys: M(1-x)M'X2 and MX(2-2x)X'(2x) (M,M'= V, Nb, Ta, Mo, or W; X,X'= S or Se) and two heterostructural alloys, Mo(1-x)WTe2 and WS2(2-2x)Te(2x). We predict four new alloys that are miscible at all temperatures: Nb(1-x)TaS2, Nb(1-x)TaSe2, VS2(2-2x)Se2x, and TaS2(1-x)Se2x. For the rest of the alloys, we present a qualitative analysis of synthesizability based on miscibility temperatures. We relate TMD size mismatch with a mixing asymmetry that indicates the synthesizability of low concentration alloys. Our results open new compositional spaces that can be used to design and synthesize TMD alloys for various applications. Acknowledgments: This work was funded by NSF DMREF-1729787.

Intrinsic Magnetic Topological Insulators in van der Waals Layer MnBi2T34-Family Materials

Yong Xu 1, 2; 1Department of Physics, Tsinghua University, Beijing, China; 2RIKEN Center for Emergent Matter Science (CEMS), Saitama, Japan.

The interplay of magnetism and topology is a key research subject in condensed matter physics and material science, which offers great opportunities to explore emerging new physics, like the quantum anomalous Hall (QAH) effect, axion electrodynamics and Majorana fermions. However, these exotic physical effects have rarely been realized in experiment, due to the lacking of suitable working materials. In this talk, we will review recent research progresses of magnetic and topological materials. In particular, we will present our recent works of finding intrinsic magnetic topological insulators in van der Waals layered MnBi2Te4-family materials [1,2]. The materials intrinsically show two-dimensional (2D) ferromagnetism in the single layer and three-dimensional (3D) A-type antiferromagnetism in the bulk, which could serve as a next-generation magnetization platform for the state-of-art research. Remarkably, we predict extremely rich topological quantum effects with outstanding features in an experimentally available material MnBi2Te4, including a 3D antiferromagnetic topological insulator with the long-sought axion states, the type-II magnetic Weyl semimetal (WSM) with simply one pair of Weyl points, and the high-temperature intrinsic QAH effect. These striking predictions, if proved experimentally, could profoundly transform future research and technology of topological quantum physics.

Reference:

Defects and Phase Transformations in 2D Materials

In Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

2D materials have unique structural mechanics [Nano Letters 15 (2015) 1302] that makes their defects and phase transformations dramatically different from those of 3D materials. I will focus on light-structure and electron-structure interactions in this talk, with a range of behaviors such as ferroelasticity [Nature Comm 7 (2016) 10843], ferroelectricity and electronic topology change [Science 346 (2014) 1344] in one to few-layer transition metal dichalcogenides. Design of ultrafast responsive 2D materials is emphasized.

Phase Polymorphism and Electronic Structures of TeSe2 and Its Ferroelectricity

Takuhisa Terfs Debe 1 and Hong Seok Kang 2; 1Institute for Application of Advanced Materials, Jeonju University, Jeonju, Korea (the Republic of); 2Department of Nano and Advanced Materials, College of Engineering, Jeonju, Korea (the Republic of).

Structure prediction complemented by density functional theory (DFT) calculation indicates that TeSe2 is the most stable among the various Te2-xSe x compounds. Different from the case of bulk Te, the material can equally adopt three different crystal structures: H2, M6, and M8 phases, which are similar to 1T-TiSe2, trigonal Te, and orthorhombic Te, respectively. These phases can be transformed from one to another by uniaxial tensile and shear stresses; they can be even transformed to their chiral mirror images. Band structure calculations including spin-orbit coupling (SOC) show that all three phases are semiconductors. The band gap (= 0.43 eV) increases with density, being the largest (= 1.86 eV) in the M8 phase with the highest density. The H2 phase exhibits hidden spin texture because of centrosymmetry. The other two phases display chiral spin texture due to the lack of the symmetry, in that two spin components of frontier bands can split by more than 100 meV in opposite directions. In addition, the layered TeSe2 possess ferroelectricity. It can be used for optoelectronic applications.

Supported Two-Dimensional Materials Under Ion Irradiation—The Substrate Governs Defect Production

Silvan Kretscmer 1, Michael Maslov 1, Sadegh Ghaderzadeh 1, Mahdi Ghorbani-Asl 1, Gregor Hlawacek 1 and Arkady Krasheninnikov 1, 2; 1Helmholtz-Zentrum Dresden, Dresden, Germany; 2Department of Applied Physics, Aalto University, Helsinki, Finland.

Ionen and electron irradiation suits particularly well for engineering the properties of nanostructures, see Refs. [1-2] for an overview. In particular, focused ion beams can be used for patterning two-dimensional (2D) materials, but the optimization of irradiation parameters requires full microscopic understanding of defect production mechanisms. In contrast to freestanding 2D systems, the details of damage creation in supported 2D materials are not fully understood, whereas the majority of experiments have been carried out for 2D targets deposited on substrates. Here, we suggest a universal and computationally efficient scheme to model the irradiation of supported 2D materials, which combines analytical potential molecular dynamics with Monte Carlo simulations and makes it possible to independently assess the contributions to the damage from backscattered ions and atoms sputtered from the substrate. Using the scheme, we study [3] the defect production in graphene and MoS2 sheets, which are two of the most important and widespread 2D materials, deposited on a SiO2 substrate. For helium and neon ions with a wide range of initial ion energies including those used in a commercial helium ion microscope (HIM), we demonstrate that depending on the ion energy and mass, the defect production in 2D systems can be dominated by backscattered ions and sputtered substrate atoms rather than the direct ion impacts and that the amount of damage in 2D materials heavily depends on whether a substrate is present or not. We also study the factors which limit the spatial resolution of the patterning process. Our results agree well with the available experimental data, provide not only insights into defect production but also quantitative information, which can be used for the minimization of damage during imaging in HIM or optimization of the patterning process.

Hexagonal boron nitride (h-BN) also known as “white graphene” is a prominent member of the 2D materials family, which has gained a significant attention for its remarkable properties in the last decade. Its superior thermal conductivity (1700-2000 W mK⁻¹), high mechanical strength (15.7 Nm⁻¹), large band gap energy (6 eV), atomically smooth surface, ultra-high flexibility, and transparency make h-BN a suitable candidate for numerous applications such as flexible and transparent electronics.

Characterization of h-BN samples has been done by XPS, UV-Vis spectroscopy, Optical microscopy RAMAN, ToF-SIMS, and SEM. XPS data confirms that the binding energy of boron and nitrogen is around 190 eV and 398 eV, respectively, which are very close to the values reported in the literature. As grown h-BN on the top surface of the foil (directly exposed to precursor flow) and on the bottom surface (confined with the quartz support) shows variable nitrogen to boron ratio. We calculated N:B ratio ranging from 0.7 to 1.11 in our samples, which clearly signifies nitrogen-rich or boron-rich h-BN regions. UV-Vis spectroscopy confirms a very sharp absorption peak near 202 nm corresponding to a bandgap of 6.13 eV.

The evolution of these morphologies is attributed to the alteration of N:B ratio evolved by the mass of the AB, which has a significant impact on the decomposition process. N:B ratio can be tuned by the decomposition monitoring of ammonia borane in order to get better control over the shape of synthesized h-BN domains. Furthermore, optimal AB decomposition conditions will be investigated by the AB mass, AB heating profile, background pressure and concentration of carrier gases to get direct access to N:B ratio.

In summary, the shape of the h-BN domains can be used as a direct indicator of nitrogen-rich or boron-rich growth. Certainly, variation in the shape of domains will influence the intrinsic and functional properties of grown h-BN layers. These results envisage that depending on the shape of individual h-BN domains, CVD synthesis will lead to either nitrogen-rich or boron-rich in-plane regions of the 2D h-BN.

References
Jingzhao Z. et al. Nanoscale DOI: 10.1039/C8NR04732D.
that induces a strong electrical polarization perpendicular to the atomic planes. As a result of the polarization, electrons and holes are spatially separated and their energies strongly reduced by the polarization field. Thus, electrical polarization plays an essential role in controlling the exciton binding energy and radiative lifetime, and can be exploited in multilayered structures to tune the luminescence to the visible from the deep to UV. This work was supported by the NSF ECCS-CDS&E program (1607796). Computational resources were provided by the DOE NERSC facility (DE-AC02-05CH11231).

9:00 AM QN01.14.02
Binary Compound Bilayer with Vertical Polarizations—Two-Dimensional Ferroelectrics, Multiferroics and Nanogenerators  Menhao Wu; Huazhong University of Science and Technology, Wuhan, China.

Vertical ferroelectricity in two-dimensional (2D) materials is desirable for high-density data storage. Herein we report the first-principles evidence of 2D vertical ferroelectricity induced by interlayer translation, which exists extensively in graphitic bilayer of BN, AIN, ZnO, MoSe2, GaSe, etc.; the bilayer of some 2D ferromagnets like MXene, VS1 and MoN2 can be even multiferroics with switchable magnetizations upon ferroelectric switching, rendering efficient reading and writing for high-density data storage. Especially, the electromechanical coupling between interlayer translation and potential can be used to drive the flow of electrons as nanogenerators for harvesting energy from human activities, ocean waves, mechanical vibration, etc.. Ferroelectric superlattice with spatial varying potential can be formed in bilayer Moire pattern upon a small twist or strain, making it possible to generate periodic n/p doped domains and shape the periodicity of the potential energy landscape. Finally, some of their multilayer counterparts with wurtzite structures like ZnO multilayer are revealed to exhibit another type of vertical ferroelectricity with greatly enhanced polarizations.

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9:15 AM QN01.14.03
Giant Spin Hall Effect in Two-Dimensional Monochalcogenides Jagoda Sławinska1; Franklin T. Cerasoli1; Haihang Wang2; Sara Postorino2; Andrew Supka2; Stefano Curtarolo3; Marco Fornari4; and Marco Buongiorno Nardelli4; 1Department of Physics, University of North Texas, Denton, Texas, United States; 2Department of Physics, Science of Advanced Materials Program, Central Michigan University, Mount Pleasant, Michigan, United States; 3Center for Materials Genomics, Duke University, Durham, North Carolina, United States.

One of the most exciting properties of two dimensional materials is their sensitivity to external tuning of the electronic properties, for example via electric field or strain. Recently discovered analogues of phosphorene, group-IV monochalcogenides (MX with M = Ge, Sn and X = S, Se, Te), display several interesting phenomena related to the in-plane strain, such as giant piezoelectricity and multiferroicity, which combines ferroelastic and ferroelectric properties. Here, using calculations from first principles, we predict for the first time giant spin Hall effect (SHE) in these materials which suggests their high potential for 2D spintronics. We reveal that the spin Hall conductivity is tunable via combinations of external strain and doping. In some configurations, the strain-induced semiconductor to metal transition enables the logic functionality of switching on/off spin currents which indicates a new route for the design of multi-tunable spintronics devices.

Acknowledgements. The members of the AFLOW Consortium acknowledge support by DOD-ONR (N00014-13-1-0635, N00014-11-1-0136, N00014-15-1-2863). MBN and FTC acknowledge partial support from Clarkson Aerospace Corporation. The calculations were performed at the Computing Center at the University of North Texas and the Texas Advanced Computing Center at the University of Texas, Austin.

9:30 AM QN01.14.04
Theoretical Investigations on Structural Stability of Two-Dimensional Ultrathin Films in Group III-V Materials Toru Akiyama, Yuya Hasegawa, Kiyoshi Koyama, Kohji Nakamura and Tomonori Ito; Department of Physics, Engineering, Mie University, Tsu-shi, Japan.

There has been increasing research interest in two-dimensional (2D) materials with honeycomb structure due to their potential applications in electronic devices. Among various 2D materials, group III-V materials such as BN with hexagonal (Hex) structure have been paid much attention. However, this is available mainly in the form of small flakes, and successful fabrication of BN thin films with large area is limited. Recently, Tsipas et al. have successfully fabricated graphene-like ADN by molecular beam epitaxy (MBE) on Ag(111) substrate. [1] They have also reported that ultrathin (sub-monolayer to 12 monolayers) AIN adopts Hex structure with larger lattice constant compared to bulk AIN with three-dimensional wurtzite (WZ) structure. Two-dimensional GaN can also be formed by migration-enhanced encapsulated growth technique using epitaxial graphene. [2] In spite of the experimental findings, there is a still open question how many layers the Hex structure is stabilized for group III-V materials. From theoretical viewpoints, we have previously investigated the stability of group-III nitrides with Hex structure by mean of density functional theory (DFT) calculations, and revealed that five-fold coordinated Hex structure is more stable than WZ structure for the films up to 15 bilayers due to interlayer electrostatic interactions. [3] In this study, we extend our approach to various group III-V materials including binary and ternary alloys. Our DFT calculations for various III-V materials (BP, AlP, GaP, InP, GaAs, AlAs, and etc.) demonstrate that they forms five-fold coordinated Hex structure and its stability depends on their ionicity: The number of layers up to which Hex structure has a lower cohesive energy than WZ structure, Lb, becomes large for III-V materials with larger ionicity. [4] Furthermore, the calculations using empirical bond-order potentials with the aid of DFT calculations [5] for B,Al,N and B, Ga, N alloys reveal that the Hex structure can be stabilized depending on the number of film thickness. The calculated Lb is also found to be dependent on boron composition of x, and the miscibility of these alloys with Hex structure is lower than those with WZ structure due to the contribution of relaxation of atoms depending on the crystal structure. These calculated results thus suggest that various 2D ultrathin films can be formed in group III-V materials. Effects of substrates such as Ag(111) and graphene on the stability of 2D ultrathin films are also examined.

References

9:45 AM QN01.14.05
Understanding Axis-Dependent Conduction Polarity in Goniopolar Layered Metals from Ab Initio Informed Tight Binding Theory Yaxian Wang, Joseph P. Heremans, Joshua Goldberger and Wolfgang Windl; The Ohio State University, Ohio, United States.

We have recently shown that NaSn2As2 exhibits opposite conduction polarities along in-plane and cross-plane directions, defined as “goniopolarity”. On the lowest level of theory, we can show that this novel phenomenon originates from a special topology of the Fermi surface, which is essentially determined by the nature of the bonding states in this layered crystal. In this paper, we present an improved fundamental understanding of goniopolarity based on a novel formulation of goniopolarity within the tight-binding model. The tight-binding matrix elements are calculated from GW calculations based on Density Functional Theory (DFT) by maximally localized Wannier functions. Considering a minimum-basis set with sp2 orbitals for both Sn and As, the 64 hopping integrals are evaluated. Within our model, we provide a new tight-binding based formulation for both Seebeck and Hall coefficients for NaSn2As2 and can show that critical ratios of hopping and on-site matrix elements exist that pose limits for goniopolarity to appear in materials. Based on that, additional candidate materials for goniopolarity can be proposed, and the design space for goniopolar materials in general will be defined.

10:00 AM BREAK
exhibit unusual polarization properties. Their in-plane piezoelectric coefficients are about two orders of magnitude larger than those of monolayer transition metal dichalcogenides and conventional bulk piezoelectric materials. Moreover, these monolayer group IV monochalcogenides are essentially spontaneously polarized and exhibit a robust in-plane ferroelectric effect above room temperature. Many of these predictions have been confirmed by recent experiments, and they also provide guidance for future applications.

11:00 AM QN01.14.07
Understanding Electrons in Flat Land for Electronic and Energy Applications
Yuanyue Liu; The University of Texas at Austin, Austin, Texas, United States.

Two-dimensional (2D) materials have great potential for many applications such as electrocatalysis and electronics. However, their developments are impeded by a number of significant challenges, many of which root in the ‘problems of electrons’. On the physics side, the electrons/holes in current 2D semiconductors do not move fast enough under electric field (i.e. low mobility), impeding their use in high-performance electronics and optoelectronics. On the chemistry side, the current 2D electrocatalysts still suffer from relatively low activity/selectivity, hindering their use in efficient energy conversion. These challenges urge for an improved understanding of the electrons in 2D materials, and using these insights to design/discover 2D host materials with better performance.

Here I will discuss our recent progress in understanding the chemistry and physics of electrons in 2D materials for electronic and energy applications. Specifically, I will show (1) what limits the intrinsic carrier mobility of two dimensional metal dichalcogenides, and how to find high-mobility 2D semiconductors [1]; (2) the significant impact of charge on electrochemical reactions of 2D materials, which is often neglected in modeling their electrochemistry, and the implications for energy applications [2].


11:15 AM QN01.14.08
Exceptional Points in Energy Spectrum of Magnetic Materials
Alexey Gaidal’, 1 and Valerii Vinokur’; 1 James Franck Institute, University of Chicago, Chicago, Illinois, United States; 2 Materials Science Division, Argonne National Laboratory, Lemont, Illinois, United States.

We investigate topological structure of complex energy surfaces of non-equilibrium magnetic systems. We consider one- and two-dimensional spin-transfer torque-driven models described by non-Hermitian Hamiltonians. The spectrum of the Hamiltonian admits branch point singularities that appear as chiral exceptional points where both eigenvalues and eigenstates coalesce. Encircling individual exceptional points in parameter space has non-trivial physical consequences resulting in non-reciprocal spin wave transfer through the system. This effect can be used in a spintronic spin filter device.

11:30 AM QN01.14.09
MXene-Based Electrode with Tunable Catalytic Activity for Oxygen Reduction/Evolution Reaction in Lithium-Air Batteries
Ali Reza Ostadhosseini, Jack Guo, Filip Simeski and Matthias Ille; Stanford University, Stanford, California, United States.

Ubiquitous applications of rechargeable batteries, particularly in portable electronics and electric vehicles, have stimulated a vigorous search for high-capacity electrode materials. In particular, Lithium-Oxygen batteries have attracted substantial attention due to their superior energy-density; yet several technical challenges must be overcome in order to enable their successful commercialization. It is well-known that the precipitation of the reaction products from the oxygen reduction reactions (ORR) during the discharge process increases the overpotential and in turn leads to reduced cyclability. MXenes are a new class of two-dimensional inorganic compounds. The versatile chemistry and the high electrical conductivity of these materials make them a prevalent candidate for catalysis. In this study, free-standing 2D titanium nitride MXene is proposed as an efficient cathode-catalyst for non-aqueous Li-O2 batteries. By performing comprehensive first-principles simulations employing density-functional theory and reactive molecular dynamics, we discovered the enhanced catalytic activity for ORR and oxygen evolution reactions (OER) through surface functionalization of MXene monolayers. Atomic-scale analysis was performed to identify the role of surface functionalization for controlling nucleation of Li2O2 and electrochemical reaction steps of ORR/OER on MXene surfaces. The free-energy pathways for adsorption of the intermediate and final products of ORR are determined, demonstrating that synergistic effects of vacancies and functionalized groups accelerate ORR by up to a two orders of magnitude compared to commonly used graphene-based cathode electrodes. These results contribute towards the design of functionalized MXene for modulating catalytic properties of ORR/OER in cathodes of Li-air batteries.

11:45 AM QN01.14.10
Bond Saturation Significantly Enhances Thermal Energy Transport in Two-Dimensional Pentagonal Materials
Zeyu Liu, Xufei Wu and Tengfei Luo; University of Notre Dame, Notre Dame, Indiana, United States.

Thermal transport in nanoscale two-dimensional (2D) materials is of great scientific interest and has practical implications for energy related applications like thermal management of energy devices, composite battery materials and on-board thermoelectric power generation for sensors. The abilities to manipulate thermal transport in 2D materials is thus highly desirable for future nano energy technologies. In this work, we identify a general rule for controlling the thermal transport in 2D pentagonal materials through bond saturation. We use first-principles calculations to investigate the phonon properties of a series of pentagonal materials, including penta-graphene (PG), hydrogenated PG (h-PG) and fluorinated PG (FPG), and find that the bond saturation of the carbon atom can modulate the bond anharmonicity and thus increase the phonon lifetime. We can follow this rule to predict very high thermal conductivity of other pentagonal structures with saturated bonds, including penta-CN2 (1027 W/mK) and two three-dimensional counterparts of PG called Tl2-carbon (819 W/mK) and AA Tl2-carbon (1049 W/mK). Moreover, similar trend of bond saturation-induced thermal conductivity enhancement can be found in other 2D pentagonal materials, such as penta-SiC2 and penta-SiN2. The results from this work unveil a general bonding-thermal transport relation for 2D materials, which can provide important guidance for designing novel materials with desirable thermal transport properties for energy applications.
Physical behaviors of 2D materials are ultimately governed by complex interactions of electrons and ions, ranging from ultrafast process at atomic scale to slow dynamics at mesoscale. Here we present our recent development of first-principles theory based on simple linear chain (LCM) and interlayer bond polarizability models. Here, we show unusual effects of strong interlayer coupling on low-frequency Raman scattering in PdSe$_2$ crystals with different number of layers. We found that the measured frequencies of the breathing modes cannot be described by a conventional LCM that treats each layer as a single rigid object. We show that strong deviations from layer rigidity can occur for the LF breathing vibrations of PdSe$_2$, which accounts for the observed disagreement with the conventional LCM. The layer non-rigidity and strong interlayer coupling could also explain the unusual strong intensities of the LF breathing modes that are comparable with those of the high-frequency Raman modes. These strong intensities allowed us to use a set of the measured LF Raman lines as unique fingerprints for a precise assignment of the layer numbers from 2 to 19. The assignment of the layer numbers was further confirmed using second harmonic generation that appeared only in the non-centrosymmetric even-layer PdSe$_2$ crystals. This work demonstrates a simple and fast approach for the determination of the number of layers in 2D materials with strong interlayer coupling and non-rigid interlayer vibrations.

Synthesis science was supported by the U.S. Department of Energy, Office of Science. Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterization and computational science at CNMS were supported by the Scientific User Facilities Division, BES.

2:15 PM QN01.15.03
Anomalous Interlayer Vibrations in Strongly Coupled Layered PdSe$_2$
Alexander Puretzky$^1$, Liangbo Liang$^1$, Akinola D. Oyedele$^1$, Yiyi Gu$^1$, Yiling Yu$^1$, Kai Xiao$^1$, Amanda V. Haglund$^1$, David Mandrus$^1$, Bobby G. Sumpter$^{1,2}$ and David B. Geohegan$^1$.$^1$Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^2$Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^3$Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

Low-frequency (LF) Raman spectroscopy has emerged as a very useful tool for characterization of the number of layers and stacking configurations in two-dimensional materials based on simple linear chain (LCM) and interlayer bond polarizability models. Here, we show unusual effects of strong interlayer coupling on low-frequency Raman scattering in PdSe$_2$ crystals with different number of layers. We found that the measured frequencies of the breathing modes cannot be described by a conventional LCM that treats each layer as a single rigid object. We show that strong deviations from layer rigidity can occur for the LF breathing vibrations of PdSe$_2$, which accounts for the observed disagreement with the conventional LCM. The layer non-rigidity and strong interlayer coupling could also explain the unusual strong intensities of the LF breathing modes that are comparable with those of the high-frequency Raman modes. These strong intensities allowed us to use a set of the measured LF Raman lines as unique fingerprints for a precise assignment of the layer numbers from 2 to 19. The assignment of the layer numbers was further confirmed using second harmonic generation that appeared only in the non-centrosymmetric even-layer PdSe$_2$ crystals. This work demonstrates a simple and fast approach for the determination of the number of layers in 2D materials with strong interlayer coupling and non-rigid interlayer vibrations.

Synthesis science was supported by the U.S. Department of Energy, Office of Science. Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterization and computational science at CNMS were supported by the Scientific User Facilities Division, BES.

2:30 PM BREAK
Molybdenum disulfide (MoS$_2$) is a promising two-dimensional (2D) semiconductor. Similar to graphite, MoS$_2$ has a layered structure comprising weak van der Waals bonding between layers, and strong covalent bonding within layers. The weak secondary bonding allows for isolation of these 2D materials to a single layer, like graphene. While bulk MoS$_2$ is an indirect band gap semiconductor with a band gap of ~1.3 eV, monolayer MoS$_2$ exhibits a direct band gap of ~1.8 eV, making it an attractive candidate for replacing Si in electronic devices. Atomic layer deposition (ALD) has been used previously to grow MoS$_2$ films using molybdenum chloride and carboxyl precursors. However, these precursors are solids at room temperature and require high temperature vapor transport. Recently, MoS$_2$ ALD using molybdenum hexafluoroide (MoF$_6$), a high vapor pressure liquid at room temperature, and hydrogen sulfide (H$_2$S) has been demonstrated. While the nucleation of MoS$_2$ during chemical vapor deposition (CVD) is understood, the nucleation of MoS$_2$ ALD using MoF$_6$ and H$_2$S on dielectric surfaces has yet to be explored. Unlike films grown by high temperature CVD, ALD MoS$_2$ is amorphous as deposited and must be annealed to crystallize the film. In this study, we utilized in situ quartz crystal microbalance and Fourier transform infrared spectroscopy measurements to investigate the first few cycles of MoS$_2$ ALD on Al$_2$O$_3$, HfO$_2$, and MgO surfaces prepared in situ by ALD. The MoS$_2$ nucleation, and in particular the effect of the first MoF$_6$ exposure, was found to depend strongly on the underlying metal oxide, the OH surface concentration, and the growth temperature. Following these in situ studies, we prepared ultrathin ALD MoS$_2$ films and subsequently annealed them in H$_2$ to crystallize the films for device measurements. Our work will provide a solid understanding of the interactions of MoF$_6$ and H$_2$S with dielectric surfaces, which is critical for the implementation of ALD MoS$_2$ in microelectronics.

Transition metal dichalcogenide (TMD) thin films are promising candidate materials in the continuing development of nanoscale devices. These materials exhibit a direct band-gap when thinned down to a single layer and also provide properties that include an improved on-off ratio and photonic application which set them apart from bulk silicon. Methods to produce wafer-scale TMD films include powder chemical vapor deposition (CVD), liquid-phase and mechanical exfoliation, metal-organic CVD, and atomic layer deposition (ALD). These methods suffer from issues with particulate contamination, pyrophoric precursors, and costly precursors along with the lack of reproducibility and layer thickness controllability. Here we demonstrate the growth of homogeneous wafer-scale mono-, bi-, and tri-layer molybdenum disulfide (MoS$_2$) using solid inorganic and liquid organic precursors in a high-vacuum environment. These samples are grown on amorphous 30-300 nm SiO$_2$ substrates and fused silica windows and without any powder or metal-organic precursors. Growth proceeds by the decomposition of carbon disulfide at a heated molybdenum filament, which yields volatile MoS$_2$ precursors that aggregate on a heated wafer. We have developed a procedure to control our thin film growth using a standard video camera from the top of the chamber to monitor the hue (0-255) of the film from the reflection of the film onto the top of the SiO$_2$. This allows controlled integer number layer thickness of our films. The continuous and homogeneous single-layer film of MoS$_2$ is deposited at wafer-scale with a total growth time of approximately an hour. Optical and electrical characterization indicates performance comparable to or better than MoS$_2$ film grown by other wafer-scale growth techniques. Our method provides a scalable process to deposit thin TMD films in a high-vacuum environment using a colorimetric hue control.

X-ray Studies of Tungsten-Based Transition Metal Dichalcogenides Narayavachari V. Kondapalli, Anusheela Das and Michael J. Bedzyk; Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States.

The demand to exploit the unique properties of 2D materials requires the synthesis of large-scale high-quality 2D materials. While epitaxial growth of 2D materials on single-crystal substrates can generate large-scale production of 2D materials without compromising the quality, it is unclear whether the 2D materials can exist as structurally and electronically distinct layers anchored by van der Waals (vdW) forces, as opposed to more strongly bound adlayers. The strength of these interactions, from weak van der Waals to strong covalent bonds, is linked to the local atomic structure of the interface. The resulting 2D materials exhibit different properties depending on the strength of the interactions with the underlying substrate.

We used x-ray standing waves (XSW) generated by Bragg diffraction from a sapphire single crystal substrate to excite X-ray fluorescence (XRF) from a 2D epitaxial layer of WSe$_2$. These measurements, performed at rotating anode and synchrotron x-ray sources, were used to find the positions of Se and W atoms relative to the substrate lattice with subangstrom resolution.

These results combined with DFT calculations could give distinct insights into WSe$_2$ and other transition metal dichalcogenides integrated epitaxially on oxide substrates. Overall, the work herein reveals how distinct X-ray surface science techniques can be used to understand questions about 2D material structure and interfaces.

Acknowledgements: NU Center for Hierarchical Materials Design (NIST 70ANB1H4H01), NU-MRSEC (DMR-1121262) and Argonne National Laboratory (DOE DE-AC02-06CH11357). The Pennsylvania State University Two-Dimensional Crystal Consortium – Materials Innovation Platform (2DCC-MIP) supported by NSF cooperative agreement DMR-1539916.

Metallo-Hydrogel-Assisted Synthesis and Direct Writing of Transition Metal Dichalcogenides Xining Zang1, J. Nathan Hohman2 and Liwei Lin3; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3University of California, Berkeley, Berkeley, California, United States.

Two-dimensional transition metal dichalcogenides (TMDs) have attracted interest for their compelling nanoscale new properties and numerous potential applications including fast optoelectronic devices, ultrathin photovoltaics, and high-performance catalysts. Large-scale growth of uniform TMD materials is essential for investigating their physics and for their integration into device. However, the wafer scale deposition of TMDs on arbitrary non-selective substrates is still beyond the current state-of-the-art. In this article, we report a method to synthesize layered TMDs (MoS$_2$ and WSe$_2$) at the wafer-scale by sulfurization of transition metal ions (Mo$^{6+}$ and W$^{6+}$) in a gelatin template (metallo-hydrogel). This process is adaptable to versatile substrates, including amorphous silicon oxide, high-temperature quartz, and silicon. Although the products are nominally few layer materials, we observe direct band photoluminescence (~1.8 eV), consistent with single- or decoupled multilayer MoS$_2$. This is attributed to the presence of surfactants included in the template.
that serve to isolate the TMDC layers electronically. Finally, the solution-based deposition enables contact printing of TMDC channels useable for device applications including thin film transistors with printed silver contacts using the same process.

### 4:45 PM QN01.16.08

**Epitaxial Growth of Antimonene-Graphene van der Waals Heterostructures**  
Matthieu Fortin-Deschenes and Oussama Moutanabbir; Polytechnique Montreal, Montreal, Quebec, Canada.

van der Waals (vdW) heterostructures display a tremendous potential as building blocks for novel nanoscale and quantum technologies. These stacks of various two-dimensional (2D) materials can exhibit a wide variety of tunable physical properties. Nonetheless, their integration in mainstream technologies is hindered by the lack of large-scale synthesis methods. In fact, most vdW heterostructures are produced by chemical transfer and yield micrometer scale heterostructures. Developing large-scale epitaxial growth processes for vdW heterostructures is therefore critical. Even though some vdW heterostructures have been produced by epitaxy, the control over their growth is remains limited and no global understanding of the vdW epitaxy mechanisms currently exist. In fact, their growth has never been observed in real-time. To address this problem, we present here an in situ low-energy electron microscopy (LEEM) study of the vdW epitaxy of antimonene-graphene vdW heterostructures on germanium substrates. Graphene was grown by Chemical Vapor Deposition (CVD) on Ge(100), Ge(110) and Ge(111). Then antimonene, a newly discovered two-dimensional material with several intriguing thickness dependent electronic and topological properties, is grown by solid-source molecular beam epitaxy (MBE) under direct LEEM observation. Nucleation of antimonene mainly occurs on small 3D nuclei which form on defects on the graphene surface. The antimonene then grows laterally to form few micrometers large flakes. The antimonene islands rarely coalesce due to competition for the precursor Sb$_4$ species. The growth morphology is strongly influenced by the Sb$_4$ deposition rate. In fact, high deposition rates (>10 nm/minute) lead to the growth of large flat islands with 3 branches, whereas lower deposition rates lead to triangular atoll-like islands with thick bands along the edges. The transition from 2D to atoll-like growth is explained based on the interplay between the growth rate, surface diffusion and edges orientation. The understanding of the vdW growth developed in this study will allow for a better control of the large-scale growth of vdW heterostructures with highly tunable physical properties.

### TUTORIAL: Defects and Magnetic Properties of Two Dimensional Materials

April 22 - April 22, 2019

Defects in crystalline solids are ubiquitous. It is the second law of thermodynamics that gives rise to the appearance of a certain amount of disorder in crystalline materials at finite temperatures. Moreover, defects can be present in synthetic materials well above the equilibrium concentration due to the imperfections in material production processes or due to the exposure of the system to irradiation with energetic particles. Such lattice imperfections have a strong influence on the electronic, magnetic, optical, thermal, and mechanical properties of the solids, normally deteriorating their characteristics. However, defects not always have detrimental effects on material properties, with the most prominent example being the doping of semiconductors by controllable introduction of impurities using ion implantation.

All of the above is relevant to two-dimensional (2D) materials, such as graphene and hexagonal boron nitride, or transition metal dichalcogenides (TMDs). It is intuitively clear that due to the reduced dimensionality the defects should have a much stronger influence on the properties of 2D materials, as compared to their bulk counterparts. Moreover, due to the morphology of 2D systems, it is much easier to introduce defects into them in a controllable manner and add new functionalities. Furthermore, the experimental realization of ferromagnetism at the monolayer level in 2D van der Waals materials beyond graphene has drawn a great deal of research interest in the recent past. In addition, these materials have exciting prospects for next generation low-power ultra-compact spintronic applications. This tutorial will review the recent developments in the rapidly growing field of defects and magnetic properties of a broad spectrum of 2D materials through a combination of theoretical and sensitive experimental approaches, and will immensely benefit scientists at all the levels.

### 1:30 PM

**Defects in 2D Materials – Theory**  
Arkady V. Krasheninnikov; Helmholtz-Zentrum Dresden-Rossendorf

In this tutorial, Krasheninnikov will present the "state of the art" in the physics of defects in two-dimensional (2D) inorganic materials with the main focus on the theoretical developments. The computational and analytical methods used in theoretical physics to get insights into defect behavior will be briefly summarized, and then the effects of impurities and point/line defects on various properties of 2D inorganic materials will be addressed. He will further discuss defect- and impurity-mediated engineering of the electronic structure of inorganic 2D materials. He will also present the results of the theoretical studies of electron-beam induced phase transformations in 2D transition metal dichalcogenides (TMDs) when electric charge, mechanical strain and vacancies are present.

### 2:30 PM BREAK

### 3:00 PM

**Defects in 2D Materials – Electron Paramagnetic Resonance Spectroscopy**  
Andre Stesmans; KU Leuven

In this tutorial, Stesmans will deal with some basic principles and methodology of the electron paramagnetic resonance (EPR) spectroscopy, outlining it as a reliable 'magnetic' technique based on non-destructively sensing of unpaired electrons, which is successfully applied in a broad range of scientific fields. Next, the attention will be directed to its application in tracing the nature of point defects, both intrinsic as well as of impurity related nature, in 2D semiconducting materials. In an exploring attitude, the latter include bulk TMD's, both of geological origin as well synthetically composed, where the research is focused on robust p-type doping by covalently bonded impurities. It will be outlined how EPR can arrive at in-depth reliable characterization of these dopants, including solid atomic identification, accurate quantification, spatial distribution, and inference of electrically key properties such as their thermal activation energy, and a fortiori, defect level(s) in the semiconductor bandgap. In combination with its outstanding selectivity, EPR takes a unique position when it comes to selectively dopant characterization on true atomic level. A separate part will deal with intrinsic defects in synthetic large-area 2D TMD layers.
in 2D magnets with dilute magnetic doping. With the goal of getting participants up to speed on this fast moving topic, the tutorial will blend a number of experimental and theoretical concepts in the topics of sample fabrication and characterization, exchange coupling in intrinsic and extrinsic magnetic systems, considerations for stability of magnetic order in 2D systems, electric field control of magnetism, spin transport in magneto-tunnel junctions, and prospects for future science and applications.

SYMPOSIUM QN02

Defects, Electronic and Magnetic Properties in Advanced 2D Materials Beyond Graphene
April 23 - April 25, 2019

Symposium Organizers
Nasim Alem, The Pennsylvania State University
Jian-Hao Chen, Peking University
Srinivasa Rao Singamaneni, The University of Texas at El Paso
Oleg Yazyev, Ecole Polytechnique Federale de Lausanne, Switzerland

Symposium Support
Army Research Office
National Science Foundation
Radiant Technologies

* Invited Paper

SESSION QN02.01: Magnetism in 2D Materials
Session Chairs: Je-Geun Park and Srinivasa Rao Singamaneni
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 128 B

10:30 AM QN02.01.01
2D Magnets—Discovery, Challenges and Opportunities Xiang Zhang; Nano-Scale Science and Engineering Center (NSEC), University of California, Berkeley, Berkeley, California, United States.

In this talk, I will present our work on 2D ferromagnet, antiferromagnet, and multi-phase interconversion. Specifically, it includes the discovery of the intrinsic ferromagnetism in 2D van der Waals materials, the new design of spin field effect transistor based on 2D antiferromagnets, and the interconversion between multiple magnetic phases in 2D magnets. These advances not only deepen the fundamental understanding of the 2D magnets physics, but also suggest possible outlets for the existing challenges in this emerging field such as high-temperature 2D magnets and low-power spintronics.

11:00 AM QN02.01.02
What Magnetic Can Teach Us About 2D Magnets Kenneth Burch; Boston College, Chestnut Hill, Massachusetts, United States.

In this talk, I will discuss the exciting theoretical possibilities for new phases that can emerge and the van der Waals materials within which they may be realized. I will focus on the utility of Raman spectroscopy for characterizing and identifying the novel aspects of the magnetic excitations in these materials.

11:15 AM QN02.01.03
Magnetic and Electrocatalytic Properties of Transition Metal Doped MoS2 Nanocrystals Jose Delgado1, Luis M. Martinez1, Christian Saiz1, Adrian Cosio1, Yanyu Wu2, Dino Villagran3, Kinjal Gandha4, Chinnathambi Karrhik4, Ilena Nebedim2 and Srinivasa Rao Singamaneni5; 1Physics, The University of Texas at El Paso, El Paso, Texas, United States; 2Chemistry, The University of Texas at El Paso, El Paso, Texas, United States; 3Arnes Laboratory, Critical Materials Institute, Ames, Iowa, United States; 4Micron School of Materials Science and Engineering, Boise State University, Boise, Idaho, United States.

In this paper, the magnetic and electrocatalytic properties of hydrothermally grown transition metal doped (10% of Co, Ni, Fe, and Mn) 2H-MoS2 nanocrystals (NCs) with a particle size 25–30 nm are reported. The pristine 2H-MoS2 NCs showed a mixture of canted anti-ferromagnetic and ferromagnetic behavior. While Co, Ni, and Fe doped MoS2 NCs revealed room temperature ferromagnetism, Mn doped MoS2 NCs showed room temperature paramagnetism, predominantly. The ground state of all the materials is found to be canted-antiferromagnetic phase. To study electrocatalytic performance for hydrogen evolution reaction, polarization curves were measured for undoped and the doped MoS2 NCs. At the overpotential of η ~ 300 mV, the current densities, listed from greatest to least, are FeMoS2, CoMoS2, MoS2, NiMoS2, and MnMoS2, and the order of catalytic activity found from Tafel slopes is CoMoS2 > MoS2 > NiMoS2 > FeMoS2 > MnMoS2. The increasing number of catalytically active sites in Co doped MoS2 NCs might be responsible for their superior electrocatalytic activity. The present results show that the magnetic order-disorder behavior and catalytic activity can be modulated by choosing the suitable dopants in NCs of 2D materials.
monolayers and multilayers [1]. The screening protocol first identifies bulk materials that appear layered according to a simple and robust chemical definition of bonding, determining then for all of these the binding energies of the respective monolayers, and their electronic state (metallic vs insulating), magnetic configuration (ferro-, ferri- or antiferro-magnetic), and phonon dispersions (to evaluate mechanically stability). Such protocol identifies a portfolio of close to 2,000 inorganic materials that appear either easily or potentially exfoliable, to be investigated further for promising properties. First focus has been on the determination of the effective masses and mobilities (from the full solution of the Boltzmann transport equation) for electronic applications; of topological invariants; of superconductivity and charge-density washes; and of photocatalytic parameters for water splitting. Thanks to the use of the AiDA (http://aiida.net) materials' informatics platform, all the high-throughput calculations can be performed and streamlined in fully searchable and reproducible ways, they are stored in a database with their full provenance tree of all parent and children calculations, and can be shared with the community at large in the form of raw or curated data via the Materials Cloud (http://www.materialscloud.org) dissemination portal.


SESSION QN02.03: Defects in 2D Materials
Session Chairs: Jian-Hao Chen, Harikrishnan Nair and Oleg Yazyev
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 128 B

1:30 PM *QN02.03.01

The research on two dimensional (2D) materials keeps attracting much interest as being propelled by compelling features like the emergence of new physical properties in the transition from bulk to the 2D aspect and the promising potential to create a multitude of innovative device structures, with the projected horizon to push beyond the boundaries of current semiconductor device technology. Among the 2D materials, layered transition metal dichalcogenides (TMDs) experience an ever-growing research interest as these could potentially replace traditional semiconductors in next generation nanoelectronic devices. Among this group of TMDs, molybdenite (MoS₂) has surfaced as a particularly interesting TMD. However, different from other semiconductors, the presence of structural defects in the 2D crystal lattice considerably affects the performance of TMD-based devices. Hence, defect identification, characterization and quantification, more specifically the evaluation of the impact of processing, is considered indispensable in the progress of device technology research. In this respect, electron spin resonance (ESR) arises as an exclusive technique for atomic assessment and quantification of point defects.

In this regard, we will present on overview of the results obtained from multifrequency ESR study of TMDs, mainly focused on MoS₂, as encountered in various forms according to origin, including p-type geological 2H MoS₂ bulk crystals, synthetic bulk 2H MoS₂ grown by chemical vapour deposition, and large-area few-layer 2H MoS₂ films grown on SiO₂ by Mo sulfurization, and metal-organic chemical vapour deposition (MOCVD) grown on c-plane sapphire template wafers after a wet transfer procedure to another substrate. The results will deal with point defects, either of intrinsic or extrinsic origin. With respect to the bulk MoS₂ crystals, a main focus has been on impurities operating as dopants. Accordingly, data will be presented on As and N impurities substituting for S sites, operating as stable, covalently bonded substitutional acceptors. Added to this are the results of one more newly-observed ESR signal, tentatively assigned to Pb impurities substituting for Mo sites, also operating as acceptors.

Besides identification of the impurity-associated defects, largely based on the uniquely revealed hyperfine structure in the ESR spectra, ESR is demonstrated as an exclusive technique for indisputable and due impurity-specific inference of the thermal activation energy (level in the bandgap) of dopants, where the As and N acceptors are found to be characterised by an activation energy of \(E_a = 0.7 \pm 0.2 \text{ meV}\) and \(45 \pm 7 \text{ meV}\), respectively.

In a final part, the work will deal with synthetic large-area polycrystalline few-layer 2D MoS₂ crystals grown on SiO₂ by Mo sulfurization or MOCVD, where the latter films are studied after layer transfer to a target thermal SiO₂/(100)Si substrate – this with the intent to probe the impact of the act of layer transfer. The large area synthetic films were found to suffer from substantial amounts of intrinsic defects: in the latter MOCVD grown films, a previously unreported signal has been observed, which based on a comparison with previous ESR data, first principles simulations, and Rutherford backscattering spectrometry data, is assigned to an intrinsic defect, most likely a Mo or MoS₂ vacancy at grain boundaries.

As to the films synthesized by sulfurization of Mo films, the presence of a previously unreported anisotropic defect of axial symmetry about the c-axis, characterized by \(g_{\perp} = 2.00145\) and \(g_{\parallel} = 2.0027\), is revealed. Based on the analysis of the ESR signal features in combination with computational results on defect g factors, the signal has been tentatively assigned to a (di)sulfur antisite defect (S or S₂ substituting for a Mo atom) with energy levels in the MoS₂ bad gap, associated with grain boundaries, the latter thus emerging as intolerably impairing the carrier mobility and layer functionality.

2:00 PM QN02.03.02
Line Defects in Two-Dimensional Transition Metal Dichalcogenides—Insights from First-Principles Calculations Arkady Krasheninnikov, \(^1,2\) Helmholtz-Zentrum Dresden, Dresden, Germany; \(^3\)Department of Applied Physics, Aalto University, Helsinki, Finland.

Line defects, such as vacancy agglomerations and grain boundaries, strongly affect the properties of 2D, see Ref. [1] for an overview. The effects can be not only detrimental, but also beneficial in transition metal dichalcogenides (TMDs), so that controlling the density and type of the boundaries in these systems should be important for engineering their properties. In my presentation, I will touch upon the energetics and formation mechanisms of mirror twin boundaries in various TMDs during their growth [2] or under electron irradiation [3,4] and post-synthesis deposition of Mo atoms [5] with the main focus on the theoretical results obtained using DFT calculations in collaboration with several experimental groups. I will then discuss how controllable introduction of mirror twin boundaries and inversion domains can be used to add new functionalities to 2D TMDs.


2:15 PM QN02.03.03
Defect-Induced Phase Transformation in Low-Symmetry 2D Materials for High Performance Electronics Kai Xiao, \(^1\) Akinola D. Oyedele, \(^2\) Shizé Yang, \(^3\) Tianli Feng, \(^4\) Yiyi Gú, \(^5\) Chenze Liu, \(^6\) Amanda Haglund, \(^7\) Alexander Puretzky, \(^8\) Gerd Duscher, \(^9\) Matthew Chisholm, \(^10\) Sokrates Pantelides, \(^11\) Christopher M. Rouleau, \(^12\) David Mandrus, \(^13\) David B. Geohegan, \(^14\) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; \(^5\) The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; \(^3\) The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; \(^14\) Vanderbilt University, Nashville, Tennessee, United States.

Two-dimensional (2D) materials especially transition metal dichalcogenides usually have diverse structural and electronic phases, which offer tremendous opportunity to explore and ultimately tailor many optoelectronic properties and quantum phenomena, including charge density waves, magnetic, topological insulators, and Weyl semimetals. However, understanding and control the phase transition process in 2D materials is still a great challenge. Our recent work shows that the defects in low symmetry 2D PdSe₂ crystals break the lattice symmetry and induce large structural distortion and ultimately form a new phase, however high symmetry 2D materials such as MoSe₂ still retain their crystalline lattice even under the defect density up to 20%. Various methods triggered the phase transformation in 2D PdSe₂ crystals will be discussed. The defect-mediated transformation process in this material was studied by using in-situ scanning transmission electron microscopy (STEM) combined with theoretical calculation. Through selective phase engineering, single material devices based on few-layer PdSe₂ crystal with the new metallic phase as the contact display the significantly enhanced electrical performance due to the reduced contact
resistance and Schottky barrier height. Our results suggest that phase engineering provides a promising way in tuning the properties in 2D materials for applications in electronics, catalysis, or magnet.

**Acknowledgment:** Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2:30 PM BREAK

3:00 PM QN02.03.04 Interfacial and Defect Engineering of 2D Materials for Optoelectronics Ashwin Ranasubramaniam; Mechanical & Industrial Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

A persistent challenge in realizing the potential of 2D materials for optoelectronics is the lack of precise control over carrier doping levels and work functions. Here, I focus on results from first-principles calculations, accompanied by complementary experiments, that seek to address these fundamental questions through various interfacial- and defect-engineering strategies. On the one hand, we explore strategies based on noncovalent functionalization of 2D materials with functional polymers that allow for spatially-targeted tuning of electronic properties of the active channel material. On the other hand, we explore strategies for small-molecule, covalent functionalization of 2D materials that result in unexpected magnetic properties with potential for spintronic applications. A common feature of the approaches proposed here is their amenability to conventional solution-processing and/or lithography that are inherently scalable for technological applications.

3:30 PM QN02.03.05 In Situ Study of Defects Produced in Free-Standing MoS\textsubscript{2} During Irradiation KoreyBurns and Assel Aiikalyeva; University of Florida, Gainesville, Florida, United States.

A number of bi-elemental two-dimensional (2D) nanomaterials (2DNMs) have been experimentally realized in recent years, including stable families of 2DNMs such as transition metal dichalcogenides (TMDs) and MX\textsubscript{2}. Unlike mono-elemental graphene, MoS\textsubscript{2} (a prototype for TMDs) consists of two atomic layers of close-packed sulfide atoms separated by one close-packed molybdenum atomic layer. TMDs exhibit a number of attractive physical properties, including electronic, optical, and mechanical. However, throughout their lifetime 2DNMs can be exposed to high temperatures and particle irradiation environments, which can dramatically alter the structure-property relationships and degrade their physical properties. This contribution seeks to understand the physical processes occurring at multiple length scales in MoS\textsubscript{2} and determine the structural stability and property evolution in MoS\textsubscript{2} in conditions far away from equilibrium. Irradiation and high temperatures push materials out of equilibrium, thus producing dynamic systems, which can result in unexpected behaviors. Defect formation and interaction mechanisms in free-standing MoS\textsubscript{2} under irradiation (and various temperatures) were observed in-situ using various experimental techniques, including high resolution transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The phenomena of interest included energy dissipation, defect formation and interaction mechanisms, and the role of defect sinks in the material’s radiation response. The irradiation response of monolayer MoS\textsubscript{2} will be compared to that of a bilayer and a material to discern the differences in their radiation response. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award # DE-SC0019014.

3:45 PM QN02.03.06 Interlayer Couplings in Tuning Magnetic Properties of Two-Dimensional Materials Wei Ji; Department of Physics, Renmin University of China, Beijing, China.

Van der Waals interactions were believed dominant for interlayer interactions in layered two-dimensional (2D) materials. We recently found wavefunction overlaps do occur at vdW gaps, namely covalent-like quasi-bonding (CLQB)[1-5]. Here, we show that such overlaps strongly affect interlayer magnetism using density functional theory calculations. In particular, the interlayer magnetic couplings (IMCs) of CrS\textsubscript{2} [6] and CrI\textsubscript{3} [7] bilayers were discussed since they are at two extremes for the strength of IMC. The interlayer FM coupling in CrS\textsubscript{2} is very robust and is nearly unable to be tuned under usual external fields, but the intra-layer magnetism does vary under layer stacking. An opposite case was found in CrI\textsubscript{3} bilayers where the intra-layer FM coupling is, however, very strong but the interlayer magnetism was found governed by a subtle change of interlayer stacking; this shows a decoupled magnetic interaction between intra- and inter-layer directions.

References

4:00 PM QN02.03.07 Contact-Free Electrical-Acoustic Characterization of Transition Metal Dichalcogenide Films Grown by Chemical Vapor Deposition Miguel Isarraraz, Ludwig Bartels and Jacob Rodriguez; Materials Science and Engineering, University of California, Riverside, Riverside, California, United States.

Surface Acoustic Waves (SAWs) and Transition Metal Dichalcogenides (TMDs), separately, are topics of current research due to their present and future use in telecommunications and beyond-CMOS technology. The interaction between a SAW and a 2D electron gas has been previously studied by measuring the absorption of the SAW by GaAs and, more recently, graphene.

Here, the interaction between a SAW and a TMD is studied using MoS\textsubscript{2} directly grown by chemical vapor deposition on 128°YX-cut LiNbO\textsubscript{3}. By focusing a 532 nm laser on the sample, the generation of electron-hole pairs is found to enhance the attenuation of the SAW as expected. We present a hybrid FET-SAW (field effect transistor-surface acoustic wave) device. Our experiments reveal close agreement between the SAW spectroscopy and the FET transport measurements. SAW spectroscopy can be used to spatially resolve variations inside triangular MoS\textsubscript{2} islands. Furthermore, the time dependence of the SAW attenuation with laser exposure is used to distinguish between semiconductor film and the substrate. This technique provides a means of electrically characterizing atomically thin semiconducting film that avoids the limitations of metallic contacts.


4:15 PM QN02.03.08 Adhesion of Pd Metal Clusters to WTe\textsubscript{2}—Binding at the Ideal and Defective Lattice Sites Yang Wang, Zdenek Dohnalek and Peter V. Sushko; Pacific Northwest National Laboratory, Richland, Washington, United States.

Robust operation of quantum devices relies on the chemical and structural stability of their parts, including electrical contacts. Given that temperatures and environmental conditions at which quantum devices are synthesized can differ dramatically from their operating conditions, it is imperative to understand how temperature variations, material imperfections, exposure to contaminants, and behavior of metal contacts are inter-related.

Here we focus on metal adhesion to a prototype 2-dimensional metal dichalcogenide WTe\textsubscript{2}, which exhibits topological behavior in a monolayer limit. We have developed a
reliable procedure to mechanically exfoliate single crystal WTe$_2$ in ultra-high vacuum in our scanning tunneling microscopy (STM) system. This approach allows for the STM images with atomic resolution to be readily acquired without further treatment. Few defects, attributed to Te vacancies, were observed. Our experiments on Pd deposition on WTe$_2$ surface show that structurally ideal sites and defects, provide stable adsorption sites for small Pd clusters (~2 nm in diameter) even after annealing to 523 K. Tip manipulation experiments demonstrate that Pd particles anchored on defects are more stable than those on non-defective surface sites: we can remove and split Pd nanoparticles above the non-defect sites using STM. The nanoparticle anchored to defects can only be altered but cannot be completely removed demonstrating a strong binding. The atomic-level insight into Pd cluster bonding to the ideal and defective sites was obtained using \textit{ab initio} (density functional theory) simulations. We discuss how the local atomic structure and charge redistribution in the vicinity of the binding site affects the stability and electronic properties of this system.

**4:30 PM QN02.03.09**

Tuning the Interlayer Properties of van der Waals Heterostructures with Substrate Surface Defects—van der Waals to Covalent Bonding Transformation Se-Yang Kim$^1$, Jung Hwa Kim$^1$, Sangwoo Lee$^2$, Jinmu Kwak$^1$, Yongse Jo$^1$, Euijoon Yoon$^2$, Gun-Do Lee$^2$, Zongheon Lee$^2$ and Soon-Yong Kwon$^1$; 1UNIST, Ulsan, Korea (the Republic of), 2Seoul National University, Seoul, Korea (the Republic of).

The physical properties of vdW heterostructures are significantly affected by their stacking geometries and interlayer coupling (including interlayer charge transfer and energy transfer). In a previous study, we showed that monolayer WS$_2$ flakes grown onto a graphene substrate exhibit outstanding air stability compared to the flakes grown on a SiO$_2$/Si substrate.$^{11}$ Using various characterization tools and based on previous reports, we demonstrated that the surface charge transfer significantly affects the prevention of air degradation for the first time. This result suggested that understanding the effect of interlayer coupling in the stacking geometry of vdW heterostructures is highly important for obtaining materials with desirable properties.

Chemical vapor deposition (CVD) has received attention for the scalable synthesis of layered 2D materials and their heterostructures. However, typically synthesized large-scale 2D films by the CVD process are polycrystalline in nature and include a high density of atomic and structural defects, which are associated with a broken lattice symmetry, a modified energy landscape, and quantum confinement. These localized heterogeneities strongly affect the electronic properties of 2D materials. Since dangling bonds at vacancy defects, curved wrinkles, and grain boundaries (GBs) are more reactive and have interaction strengths different from that of a pristine region, defects in the template layer can have a profound effect on the nucleation and growth of heterostructures. However, the effects of atomic and structural defects on the interlayer properties or configuration have not yet been considered; instead, previous theoretical and experimental studies have considered only defect-free templates.

In this study, we demonstrate that the intrinsic properties of subsequent layers of a vdW heterostructure are based on the structural features of the template layer (e.g., the basal plane of graphene), using two types of WS$_2$ flakes grown directly on graphene defects (D-WS$_2$) and a pristine basal plane (B-WS$_2$). Both types of WS$_2$ flakes have the same crystal structure despite the atomic displacement and lattice distortion beneath the D-WS$_2$ flakes; however, they strongly influence the interlayer interactions between the stacked layers, thus affecting the layer deformability, thermal stability, and physical and electrical properties. Combined experimental and computational studies showed that the difference in the behavior of D-WS$_2$ flakes could be attributed to the formation of covalent bonds via W atomic bridges (i.e., formation of larger overlapping hybrid orbitals) at defect sites. Our results reveal the importance of understanding the interlayer coupling in stacking geometries and its correlation effect for designing desirable properties in 2D vdW heterostructures.


**4:45 PM QN02.03.10**

Atomic Structure, Stacking Order and Electronic Structure of Two-Dimensional III-VI Alloys Amin Azizi$^{1,2}$, Gabriel Antonius$^1$, Emma Regan$^{1,2,3}$, Rahmatollah Eskandari$^1$, Salman Kahn$^{1,3}$, Feng Wang$^{2,5}$, Steven Louie$^{1,3}$ and Alex Zettl$^{1,2,3}$; 1Department of Physics, University of California at Berkeley, Berkeley, California, United States; 2Kavli Energy Nanoscience Institute, University of California at Berkeley, Berkeley, California, United States; 3Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Alloying two-dimensional (2D) semiconductors provides a powerful method to tune their physical properties, especially those relevant to optoelectronic applications. Visualizing the atomic-scale crystal structure of multielemental materials is crucial in order to correlate their structures-property relationship and engineer their functionality. However, constructing the atomic structure of alloys becomes more difficult as the number of atomic planes and atomic species in an alloy increases. Here, we reveal structural information about the atomic lattice of monolayer and few-layer III-VI alloys using annular dark-field scanning transmission electron microscopy (ADF-STEM) imaging combined with image simulation, second harmonic generation (SHG), and first principles calculations. In addition, we correlate the atomic and electronic structure of the alloys and probe change in their electronic structure as a function of layer number using low-loss electron energy loss spectroscopy (EELS) and density functional theory (DFT) calculations.

8:00 AM *QN02.04.01*

Understanding Properties of Advanced Two-Dimensional Materials Based on Low-Voltage Atomic Scale TEM Experiments Ulre Kaiser; Central Facility of Materials Science Electron Microscopy, University of Ulm, Ulm, Germany.

To obtain structural and electronic properties of advanced two-dimensional material at the atomic scale is a growing demand in materials science. A new type of transmission electron microscope operating at electron energies between 80keV and 20keV has been developed. It allows to undercut most of the materials knock-on damage thresholds and enables sub-Angstrom resolution in an 4000x4000 pixels, single-shoot image down to 40keV by correcting not only the geometrical aberrations of the objective lens but also its chromatic aberration [1,2]. During the imaging process, the interaction of the beam electrons with the low-dimensional material can, nevertheless, result in changes of the atomic structure due to ionization and radiolysis [3], and sophisticated sample preparation methods are employed to reduce these effects [4,5]. We briefly outline key instrumental and methodological developments.

To modify properties of two-dimensional materials, we use the electron beam not only for imaging its original structure but also for engineering new properties. Thus we report on the structure as well as on electron-beam-induced transformations from point to extended defects in 2H-MoTe$_2$ and their changes to the distorted 1T-MoTe$_2$ phase. In the case of TaSe$_2$, we demonstrate the creation of commensurate charge density wave (CDW) in a monolayer 1T-TaSe$_2$, and show in addition that the CDW’s order varies due to an increase in the S/Se vacancies. For the two-dimensional material MnPS$_2$, we show that EELS experiments provide a means to identify single-layer MnPS$_2$ from bulk structures and give the signature of the low dimensionality in their electronic excitations [7]. Finally we intercalate bilayer graphene by lithium and study the lithiation and delithiation between bilayer graphene, as well as the structure of the new high density crystalline Li-Phase [8].

Most of our studies are accompanied by first principle calculations to understand the structural and electronic properties. [9].

Critical Behavior and Magnetocaloric Effect in CrI

8:30 AM *QN02.04.02
Properties of Monolayer Vanadium Dichalcogenides Grown by Molecular Beam Epitaxy

Matthias Batzill
University of South Florida, Tampa, Florida, United States.

Ferromagnetic ordering in monolayer vanadium dichalcogenides was predicted by DFT, despite the lack of ferromagnetic ordering in its bulk form. Ferromagnetic 2D materials with high Curie temperatures are highly sought to enable spintronic devices based on van der Waals heterostructures. In this talk we present a discussion of VSe$_2$ and VTe$_2$ monolayers grown by molecular beam epitaxy and study the difference of their monolayer properties compared to the bulk. In addition, to charge order states and structural variations of the monolayer and the bulk, we critically assess the origin of the measured ferromagnetic properties [1] in (sub)monolayer VSe$_2$.


9:00 AM QN02.04.03
Magnetic Characterizations of Proton Irradiated van der Waals Magnets CrSiTe$_3$

Luis M. Martinez$^{1}$, Yu Liu$^{2}$, Cedomir Petrovic$^{2}$, Lin Shao$^{2}$ and Srinivasa Rao Singamaneni$^{1}$
$^{1}$Physics, The University of Texas at El Paso, El Paso, Texas, United States; $^{2}$Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York, United States; $^{3}$Nuclear Engineering, Texas A&M University, College Station, Texas, United States.

Magnetic van der Waals (vdWs) crystals have gained a great deal of attention in the recent past owing to their attractive layer-dependent anisotropic magnetic properties, and for next generation low power spintronic applications. Irradiation with high energetic particles such as protons is an effective route to manipulate the magnetic properties of these materials. In this work, we present the magnetic properties of proton irradiated (10$^{15}$/cm$^2$) vdWs crystal, namely, CrSiTe$_3$ (CST). Pristine CST is a ferromagnetic (Curie temperature, T$_C$ = 32 K) semiconductor (band gap = 0.7 eV). The magnetic measurements were performed both in-plane (IP) and out-of-plane (OOP) geometry as a function of temperature and magnetic field. Most significantly, at 2 K, the IP saturation magnetization increased from 3.85 to 4.77 $\mu_B$ upon proton irradiation. Furthermore, proton irradiation causes an increase in the coercive field (H$_C$) from 465 to 542 Oe and remnant magnetization (M_r) from 0.783 to 1.375 $\mu_B$. In OOP geometry, due to proton irradiation, both H$_C$ (from 138 to 223 Oe) and M_r (0.0493 to 0.247 $\mu_B$) have increased, and noticeable (168 Oe, 1 K) an exchange bias is observed. No significant change in T$_C$ is noted upon proton irradiation. The temperature dependent (10-50 K) X-band (~9.43 GHz) electron paramagnetic resonance (EPR) measurements performed on both pristine and proton irradiated CST crystals show a strong modification in the EPR signal shape from Dysonian to Lorentzian—inferring that the magnetic (super) exchange interactions and electronic behavior are altered. We will present and discuss our comprehensive experimental findings and offer plausible explanation for the observed behavior.


9:15 AM QN02.04.04
Magnetic Frustration and Antiferromagnetism in Saw-Tooth Lattice Mn$_2$SiS$_4$-xSex (x = 0 - 4) Chalcogenides

Hariharan Nhalil$^{1}$, Raju Baral$^{1}$, Adrian Cosio$^{1}$, Bethuel O. Khamala$^{1}$, Srinivasa Rao Singamaneni$^{1}$, Magdalena Fitta$^{2}$, Rajendra R. Zope$^{2}$, Tunna Baruah$^{2}$, Daniel Antonio$^{2}$, Krzysztof Golfryk$^{2}$, Bayrammurad Saparov$^{2}$ and Harikrishnan S. Nair$^{1}$
$^{1}$The University of Texas at El Paso, El Paso, Texas, United States; $^{2}$Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, Oklahoma, United States; $^{3}$The Henryk Niewodniczanski Institute of Nuclear Physics - PAN, Krakow, Poland; $^{4}$Idaho National Laboratory, Idaho Falls, Idaho, United States.

The olivine A2BX4 are potential candidates for thermoelectric and magnetic applications. An orthorhombic Pnma symmetry is adopted by A2BX4 where the A site forms a triangle-based low dimensional saw-tooth chain. In the present work, we have studied Mn$_2$SiS$_4$-xSex (0 < x < 4) using magnetization, specific heat, thermal conductivity and density functional theory. In general, the compounds undergo antiferromagnetic transitions and display spin-flip transition upon application of magnetic field. The TN shows a linear decrease from 86 K for Mn$_2$SiS$_4$ towards 66 K for Mn$_2$SiSe$_4$ as x varied, whereas the critical field for spin-flip varied non-linearly. The specific heat of Mn$_2$SiS$_4$-xSex revealed very low magnetic entropy at the TN thereby bringing out the underlying frustrated nature of the Mn$^2+$ ions in the saw-tooth lattice. The density functional theory calculations show an energy gap of 0.5 eV between the valence and conduction bands and accordingly, a semiconducting-like thermal conductivity is revealed by the olivines. Our results are explained based on the emergence of frustration in the triangular units of the saw-tooth Mn lattice.

9:30 AM QN02.04.05
Magnetism and Chemical Disorder in van der Waals Bonded Crystals

Michael McGuire; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

I will discuss examples of chemically disordered materials recently studied in our laboratory, with a focus on crystallographic and magnetic behaviors in bulk crystals of cleavable, layered halides and chalcogenides. In several cases, both x-ray diffraction and atomic resolution electron microscopy were key in understanding the average structure, local disorder, and defect ordering. Much of the work is motivated by efforts to move toward higher magnetic ordering temperatures, and to achieve stronger magnetic anisotropy by incorporating more spin orbit coupling. With these aims in mind, the target materials include metallic systems with strong magnetic interactions and insulating compounds with 4d and 5d transition metals.

10:00 AM BREAK

10:30 AM *QN02.04.06
Gate-Tunable Room-Temperature Ferromagnetism in Two-Dimensional FeGeTe$_2$

Yuanbo Zhang and Yujun Deng; Fudan University, Shanghai, China.

The advent of two-dimensional van der Waals crystals creates new possibilities in developing novel spintronic devices. Recent experiments have demonstrated that it is possible to obtain two-dimensional ferromagnetic order in insulating Cr$_2$Ge$_2$Te$_5$ and CrI$_3$ at low temperatures. Here, we developed a new device fabrication technique, and successfully isolated monolayers from layered metallic magnet Fe$_3$GeTe$_5$. We found that the itinerant ferromagnetism persists in Fe$_3$GeTe$_5$ down to monolayer. The ferromagnetic transition temperature, T$_C$, is suppressed in pristine Fe$_3$GeTe$_5$ thin flakes. An ionic gate, however, dramatically raises the T$_C$ up to room temperature. The gate-tunable room-temperature ferromagnetism in two-dimensional Fe$_3$GeTe$_5$ opens up opportunities for potential voltage-controlled magnetoelectronics.

11:00 AM *QN02.04.07
Critical Behavior and Magnetocaloric Effect in CrI$_3$ and Cr$_2$Ge$_2$Te$_5$

Yu Liu and Cedomir Petrovic; Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York, United States.

Layered intrinsically ferromagnetic (FM) semiconductors hold great promise for both fundamental physics and future applications in nanospintronics [1-5]. CrI$_3$ and Cr$_2$Ge$_2$Te$_5$ have recently attracted wide attention since long-range ferromagnetism persists in atomically thin devices due to large magnetocrystatalline anisotropy [5-7]. In this talk we will discuss the nature of the FM transition in bulk crystals based on a detailed study of the critical properties and scaling analysis of magnetic entropy change. The obtained critical exponents suggest three-dimensional (3D) long-range magnetic coupling in CrI$_3$ and two-dimensional (2D) Ising-like type coupled with a long-range interaction in Cr$_2$Ge$_2$Te$_5$ [8,9]. The rescaled magnetic entropy changes collapse onto a universal curve independent of temperature and field for both materials, confirming a second-order type of the magnetic transition [10,11]. Considering its ferromagnetism can be maintained upon exfoliating bulk crystals down to a single layer, further investigation on the size dependence of critical properties and magnetocaloric effect is of high interest.

Acknowledgements

This work has been supported by the Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences as part of the Computation Material Science Program (Y.L. and C. P.) and by the U.S. DOE under Contract No. DE-SC0012704 (C.P.).
The recent discovery of 2D magnets provides new ways to study 2D magnetism by harnessing the unique features of atomically-thin materials, such as electrical control for magnetoelectronics and van der Waals (vdW) engineering for novel interface phenomena. In this talk, I will describe our recent magneto-optical spectroscopy experiments on vdW magnets. I will discuss the layered antiferromagnetic properties of CrI3 with electrical control, giant tunneling magnetoresistance through spin filtering effect in vdW magnetic tunnel junctions, magnetic dynamics in zigzag antiferromagnets, and progress on exfoliable 2D magnets with stable magnetic order near room temperature.

SESSION QN02.05/QN01.06/QN03.08: Keynote: Joint Session: 2D Magnets and Heterostructures
Session Chair: Srinivasa Rao Singamaneni
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 129 A

2:00 PM *QN02.06.02
The Origin of Single Photon Emission in 2D WSe$_2$
Yu Jie Zheng$^1$, Lan Wang$^2$, Cheng Tang$^3$, Changgu Lee$^4$, Gian Nguyen$^5$ and An-Ping Li$^6$; $^1$Sungkyunkwan University, Suwon Gyonggi, Korea (the Republic of); $^2$RMIT University, Melbourne, Victoria, Australia; $^3$Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Several experimental groups have shown that defect structures in 2D WSe$_2$ result in single photon emission (SPE). However, the origin of SPE is still unknown. We present a first principles study of the nature and optical properties of point defects in 2D WSe$_2$, together with scanning tunneling microscopy (STM) and scanning transmission electron microscopy images. We predict that O$_{ins}$ can dissociate easily at Se vacancies, resulting in O-passivated Se vacancies (O$_{pass}$) and O interstitials (O$_{int}$), which give STM images in good agreement with experiment. Our GW-Bethe-Salpeter-equation calculations show that O$_{pass}$ defects give exciton peaks $\sim 50$–100 meV below the free exciton peak, in good agreement with the localized excitons observed in independent SPE experiments. No other point defect (O$_{ins}$, Se vacancies, W vacancies, and Se$_x$ antisite defects) gives excitons in the same energy range. We conclude that the O$_{pass}$ defect is a likely source for the SPE previously observed in 2D WSe$_2$.

SESSION QN02.06: Theory and Other Physical Properties of 2D
Session Chairs: Matthias Batzill, Srinivasa Rao Singamaneni and Oleg Yazyev
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 128 B
Three-dimensional (3D) topological insulators (TIs) have emerged as an important class of materials for realizing novel quantum phenomena. Doping 3D TIs with various elements, both magnetic and non-magnetic, has played a vital role in improving the quality of 3D TIs and/or manipulating their surface states for novel quantum phenomena. The success of this strategy has been manifested in seminal observations of the quantum anomalous Hall effect and the quantum Hall effect in doped TIs. In this talk, however, we would like to demonstrate that complications could arise from the doping with two TI systems. One is the (Bi,Sn)Te$_3$, in which strong electrostatic fluctuations lead to formation of electron-hole puddles and a sublinear power law temperature dependence of the electron dephasing rate [1]. The other is Mn-doped Bi$_2$Se$_3$, in which the spin structure of its ground states has been controversial and new insights could be gained from our recent observation of a two-component anomalous Hall effect [2].

This work was supported by MOST, NSFC and CAS.

References

4:00 PM QN02.06.05
Electronic Structure of Single and Double Transition Metal MAX Phases and MXenes Weiwei Sun$^{1,2}$, David Mullins$^3$, Michael Naguib$^1$ and Paul Kent$^{1,4}$; $^1$Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^2$Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; $^3$Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana, United States; $^4$Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

MXenes are a large family of conducting two-dimensional (2D) materials, synthesized by the chemical etching method using acids such as HF or HCl from their parental ternary carbides MAX phases, where M stands for transitional metal elements, A stands for the A group elements, and the X is either C or N. [1-3] MXenes show great promise for the usage of supercapacitors, in part due to pseudocapacitance induced by the reversible surface binding processes. [4-5] However, a comprehensive investigation of the valence and oxidation state changes is still lacking.

In this work, by means of X-ray absorption spectra (XAS) and density functional theory (DFT), we have systematically investigated the valence states of a series of Ti, Mo containing Ti$_3$AlC$_2$ (Ti$_3$C$_2$T$_x$), Ti$_3$MoAlC$_2$ (Ti$_3$MoC$_2$T$_x$) as well as Ti$_3$Mo$_2$AlC$_3$ (Ti$_3$Mo$_2$C$_3$T$_x$), where T stands for terminations, e.g. O. F. Experimentally, the low-dimensional MXenes exhibit greater valence states for metal atoms compared with those in their parent bulk MAX phases. The increasing thickness of the M-X blocks suppresses the valence states of Ti atoms. Our DFT calculations employed special quasi-random structures (SQS) for bcc (Mo) and central metal (Ti) layers. We also tested a variety of density functionals to locate the most suitable one to describe the structure and the chemical bonding, including the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation, [7] Van der Waals corrections, [8] and the Hubbard U correction for the localized d electrons in Ti/Mo. [9] We determine that the intermixing as well as the Van der Waals corrections play significant roles on the structural and electronic properties, which effectively tunes the oxidation state. Including all of these effects leads to the agreement with our experimental observations and suggests that the synthesized MXenes also has significant intermixing. The unveiled tendencies of alloying, varying the thickness, dimensionality and surface terminations give insight to the measured capacitive properties of these materials.

References
type. Finally, relaxation of the localized GHz modes to the excitation of low-frequency (MHz) whole-flake oscillations emerges as cantilever-type dynamics in the microsecond UEM image sequence. Altogether, these results produce a comprehensive picture of the effects of local structure and morphology on the excitation and decay of coherently phonon modes in multilayer MoS₂.


Symmetry, interaction and topological effects greatly influence the quantum properties of atomically thin two-dimensional (2D) materials. Defects and environmental screening can play equally important roles in determining their behaviors. In this talk I present several interesting phenomena related to point defects and substrate screening on the properties of 2D materials. 1) We study, using ab initio GW-BSE theory, the effect of point-defect chalcogen vacancies on the optical properties of monolayer transition metal dichalcogenides (TMDs). The chalcogen vacancies introduce unoccupied in-gap states and occupied resonant quasiparticle defect states. These defect states give rise to strongly bound defect excitons and hybridize with excitons of the pristine system, reducing the valley-selective circular dichroism. The results suggest a pathway to tune spin-valley polarization and other optical properties through defect engineering. 2) A fascinating property of monolayer semiconductors is that the electronic bandgap ceases to be an intrinsic physical parameter and can be engineered through the surrounding dielectric environment. We have exploited such a dielectric-dependent electronic bandgap and demonstrated the formation of a lateral heterojunction within a homogeneous MoS₂ monolayer through substrate engineering. The capability to tailor the local band structure and electrical transport in 2D semiconductors through dielectric engineering can open exciting new ways to design 2D nanoelectronic and optoelectronic devices. 3) Plasmons in atomically thin 2D materials are distinct from those of the bulk and traditional 2D electron gas systems. We discover that the plasmon dispersion in real quasi-2D metals is qualitatively different, being virtually dispersionless for wavevectors of typical experimental interest. This stems from a lack of continuous translational symmetry, making dispersionless plasmons a universal phenomenon in quasi-2D metals. Moreover, our ab initio calculations show that plasmons on monolayer metallic TMDs are long lived and localizable in wave packets (within ~15 nm) which does not significantly disperse over practical measurement time. Their slow propagation opens the possibilities of tracking plasmon wave packets in real time and of localizing long-lived, boson-like excitations in extended, atomically thin materials.

This work was supported by the U. S. Department of Energy, National Science Foundation, and Office of Naval Research. I would like to acknowledge collaborations with members of the Louie group.

Electron Spin Resonance Properties of CrI₃ and CrCl₃ Single Crystals Christian Saiz₂, Michael McGuire¹, Johan van Tol¹ and Srinivasa Rao Singamaneni³; ¹University of Texas at El Paso, El Paso, Texas, United States; ²Florida State University, Tallahassee, Florida, United States; ³Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The discovery and subsequent research excitement of new van der Waals magnetic semiconductors such as CrI₃ and CrCl₃, in the post silicon era, offers novel applications in computing and data storage due to the unexpected magnetic properties associated with the reduced dimension and layered structure. Electron spin resonance (ESR) spectroscopy is an ideal local experiment that can pinpoint the atomic origin and underlying mechanisms of magnetic interactions in these materials. This work presents our recent experimental findings on ESR investigations in these compounds as a function of temperature (5-500 K) and microwave frequency (9.43 and 120 GHz). The temperature dependences of the ESR line width and g-value show clear magnetic phase transitions at 61 K and 17 K, in the case of CrI₃ and CrCl₃, respectively. These results are consistent with magnetization and heat capacity data. For CrI₃ at room temperature, the estimated g-value from the single Lorentzian signal is 1.986 and peak-to-peak line width (ΔHpp) is 336 Gauss (G). In the case of CrCl₃, the estimated g-value is 1.986 and ΔHpp is 82 G. These are the benchmark signatures of Cr⁺⁺(S = 3/2) ions in the octahedral site where all the three spins are in the t2g state, which are responsible for the magnetic behavior of this compound. Interestingly, the ESR signal appearing from CrCl₃ is narrower by a factor of four, which is a direct consequence of different magnetic exchange interaction strengths between CrCl₃ and CrI₃ single crystals. This is due to the more coherent nature of the interactions of Cr⁺⁺ with iodine than with chlorine. This observation not only confirms the presence of Cr⁺⁺ ion, but also shows the effect of halide ion on the magnetic interaction of these layered compounds. In addition, we will also present light-induced ESR properties of these materials.

Magnetic Properties of Proton Irradiated van der Waals Fe₂₋₃GeTe₂ Adrian Cosio¹, Ruhvyan Olmos¹, Luis M. Martinez¹, Yu Liu², Cedomir Petrovic², Lin Shao¹ and Srinivasa Rao Singamaneni³; ¹Physics, The University of Texas at El Paso, El Paso, Texas, United States; ²Condensed Matter Physics and Materials Science, Brookhaven National Lab, Upton, New York, United States; ³Nuclear Engineering, Texas A&M University, College Station, Texas, United States.

There has been an intense research interest in exploring the magnetic properties of van der Waals (vdWs) crystals owing to their interesting layer-dependent anisotropic magnetic properties. These materials are expected to show great potential for next generation low power spintronic applications. Proton irradiation is an effective route to manipulate the magnetic properties of these materials. In this work, we present the magnetic properties of proton irradiated (10⁶ cm⁻²) Fe₂₋₃GeTe₂ (FGT) single crystal. FGT is a strongly correlated ferromagnetic metal with a Curie temperature (Tc) of 151 K, which is confirmed through magnetization vs. temperature (M(T)) and heat capacity measurements. The effective moment for pristine FGT was found to be μeff = 5.84 μB for H//ab and 5.81μB for H//c. After proton irradiation, FGT displays the same behavior as the pristine M(T) measurement and exhibits a slight increase in the effective moment to 5.99 μB (H//ab) and 5.95 μB (H//c). The isothermal magnetization for pristine FGT shows the c-axis as the easy axis for both pristine and irradiated FGT. A slight increase is observed in the magnetization saturation after proton irradiation from Ms = 1.044 μB/Fe (H//c) and 0.9535 μB/Fe (H//ab) to Ms = 1.0867 μB/Fe (H//c) and 0.9796 μB/Fe (H//ab). Heat capacity (HC) measurements were also performed on pristine and irradiated samples. Both samples exhibit a
clear peak at 151 K, which is consistent with the PM-FM transition. The magnetic heat capacity, which was obtained by subtracting the phonon contribution using the Einstein model, was used to derive the magnetic entropies. The obtained entropies were ~0.153 J mol\(^{-1}\) K\(^{-1}\) for pristine and ~0.198 J mol\(^{-1}\) K\(^{-1}\) for irradiate samples. Electron Paramagnetic Resonance studies have also been performed on both the crystals to better understand the effects of proton irradiation on an atomic level. We will present and discuss our comprehensive experimental findings.

QN02.08.03

Solution-Processable Method for Producing High-Quality Reduced Graphene Oxide Displaying ‘Self-Catalytic Healing’  
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Reduced graphene oxide (rGO) has potential as a mass-productive and cost-effective substitute for graphene, but displays poor crystal quality due to various types of structural defects. Though many attempts have been reported to improve the quality of rGO, most of them require sophisticated equipment or severe conditions such as toxic chemicals, high temperature, and electron beam or plasma treatment in ultra-high vacuum (UHV) conditions. Here, we report a mild and simple solution-based healing method for obtaining high-quality rGO using this method involving the use of a simple camera flash light treatment and the nonreactive chemicals such as acetic acid and ethanol. Exposing a GO solution containing L-ascorbic acid and ethanol to the flash light irradiation for a short amount of time (<10 min) resulted in the formation of rGO displaying high quality both with respect to its chemical composition and morphology.

To elucidate the mechanism of the flash-light-induced healing of rGO, we acquired and analyzed the transient absorption spectrum for the healing reaction by using femtosecond pump-probe spectroscopy; this analysis revealed the photo-catalytic activity of GO by itself to repair chemical and topological defects, and we hence named this process ‘self-catalytic healing’.

QN02.08.04

Synthesis of Amorphous 2D Metal Oxides and Hybrid Organic-Inorganic Films  
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2D materials are frequently derived from layered crystalline materials, however bottom-up syntheses present the opportunity to explore amorphous 2D materials with high defect densities. The high concentration of defects along the surface of amorphous 2D materials suggests unique transport properties like faster ion diffusion kinetics than crystalline 2D materials. We report the synthesis of amorphous thin films via Atomic Layer Deposition (ALD) and substrate dissolution. Here, we show 5 nm thick films with lateral sizes up to 1 mm composed of Al\(_2\)O\(_3\), HfO\(_2\), ZrO\(_2\) and multilayer metal oxides via this method. The quality of film growth depends on the surface of the NaCl substrate, where extended exposure to ambient environment promotes a transition to continuous growth from island growth, as observed for freshly cleaved crystal faces. Unlike some strong chemical etchants frequently used in nanomaterial synthesis, our aqueous dissolution of the NaCl substrate is compatible with many nanomaterials. In addition to large area films, we apply this approach to high surface area NaCl powder substrates to produce a large quantity of metal oxide nanomaterials with inexpensive substrates and gentle aqueous etching. We demonstrate the tunability of the surface chemistry by functionalizing films with organic self-assembling monolayers (SAMs), like alkanolic acids and fluorosilanes. The functionalization of the surface of the metal oxides contributes to the development of a new class of hybrid organic-inorganic amorphous 2D materials. The structure of amorphous 2D materials suggests future applications as membrane materials to with fast diffusion rates and control of ion selectivity.

QN02.08.05

Olivine Mn\(_2\)Si\(_3\)O\(_6\), So—Magnetic Frustration and Spin-Flop Transition in Triangular Sawtooth Lattice  
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Due to their profitable band structure features, olivines are potential candidates for thermoelectric and photovoltaic applications. In the present work we study the magnetic properties of sawtooth lattice olivine Mn\(_2\)Si\(_3\)O\(_6\) by replacing Si with Se progressively. We study the spin flop antiferromagnetic transition in the composition series, Mn\(_2\)Si\(_3\), Mn\(_2\)Se\(_3\), (x = 0 – 4). The magnetic phase transition occurred at 86 K for x = 0 compound and reduced almost linearly in magnitude as Se-doping increased. New magnetic anomalies below 20 K are identified for all these compounds through the present work, which might correspond to spontaneous spin re-orientations. The magnetic phase transitions characterized using specific heat revealed very low magnetic entropy at transition temperature for the x = 0 compound, which suggested that the underlying frustrated nature of the Mn\(^{2+}\) ions was in the sawtooth-like triangular arrangement. The spin-flop transition occurred at critical field of 2.7 T for x = 0 and evolved with the composition in a non-linear fashion. Our studies mark the maximally frustrated compound as the x = 4. Our density functional theory calculations point towards the existence of competing magnetic interactions in the triangular units of Mn as leading to frustration effects.

QN02.08.06

Magnetic Instabilities in Low-Dimensional Co\(_{0.75}\)Mg\(_{0.25}\)Ta\(_2\)O\(_6\) Trirutile  
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Using a combination of experiments and density functional theory (DFT) calculations, we probe the magnetic ground state of the low dimensional anisotropic ising-like system, Co\(_{0.75}\)Mg\(_{0.25}\)Ta\(_2\)O\(_6\) (x = 0, 0.1, 0.3, 0.5, 0.7, 1). Neutron diffraction data was collected at the high resolution neutron powder diffractometer (PSD) at MURR, Missouri. Co\(_{0.75}\)Mg\(_{0.25}\)Ta\(_2\)O\(_6\) adopts the tri-rutile space group P42/mnm in the whole composition range and does not undergo structural changes. Co\(_{0.75}\)Mg\(_{0.25}\)Ta\(_2\)O\(_6\) displays an antiferromagnetic ordering occurring below 6 K. For the x = 0 we observe additional low temperature magnetic transitions. With progressive Mg-doping the magnetic transition disappears and gives rise to short-range correlations with an enhancement in ferromagnetism. Our neutron and specific heat data neatly captures these features of low-dimensional magnetism. We performed DFT calculations with the full-potential local-orbital (FPLO) code using the generalized-gradient approximation (GGA) in the Perdew-Burke-Emzerhof (PBE) scheme. From DFT, the magnetic ground state is found to be ferromagnetic (FM) with the lowest energies among four different magnetic configurations within GGA. However, the small energy difference between the FM and first excited AFM state (\(\pm 15\) meV) is indicative of competing ground state. Here we report results for the FM state where band gap of 0.4 eV was found between the \(d_{xz}\) states in spin-down channel within GGA while that with U = 5 eV for Co, gap rises to ~3.0 eV. Further work is in progress to confirm the antiferromagnetic ground state as found in experiment.

QN02.08.07

Defect Dominated Trion Dynamics in Monolayer WS\(_2\)  
Paul D. Cunningham, Kathleen M. McCreary, Aubrey T. Hambicki and Berend Jonker; U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Weak screening of Coulombic interactions lead to strong many-body interactions in monolayer transition metal dichalcogenides (TMD). This gives rise to the formation of tightly bound excitons, many-body particles such as biexcitons, many-body scattering mechanisms such as exciton-exciton annihilation,\(^1\) and screening effects such as bandgap renormalization.\(^2\) Charged trions, where an exciton couples to a charge carrier, have been observed in the emission spectra of unintentionally doped TMDs and may form due to defect trapping of charge carriers in those materials. Recently, it was shown that adsorbed molecules can passivate defects in TMDs. Specifically, WS\(_2\)can be thermally or laser annealed in vacuum to remove atmospheric adsorbates and reveal trion emission;\(^3\) excitonic emission is restored under dry air flow. This is likely due specifically to adsorbed oxygen,\(^4\) which may bind to defect sites in the crystal lattice and neutralize their net charge. It is possible that these defect sites are the same sites responsible for regions of weak emission that have been universally observed in WS\(_2\).\(^5\) Interestingly, this annealing process can only be done for transferred monolayers indicating that strain in as-grown layers prevents this process.\(^1\) Here, we report the ultrafast dynamics of the trions in WS\(_2\). We use the aforementioned annealing process to remove atmospheric adsorbates from defect sites, effectively doping
the WS$_2$ and allowing for excitation of trions. We show that after annealing the trion absorption resonance appears in the ground state absorption spectra in addition to the typical A-exciton peak. We estimate the trion binding energy as 32 meV. In dry air, we see only the A-exciton resonance, which shows that oxygen and water vapor is responsible for neutralizing defect sites. Ultrafast transient absorption spectroscopy shows that excitons dissociate rapidly into trions. The decay of the photoexcited trions does not appear consistent with many-body Auger mechanisms, but instead appears to be dominated by trapping. We discuss the prospects for using annealing as a methodology for preparing trions states for studies targeting their valley polarization and valley lifetime. We conclude that while this is an effective means of creating trions for fundamental studies that ultimately the trap-limited lifetime may limit the usefulness of such states.

References:

QN02.08.08

Electrical Conductivity of Stabilized Bilayer Graphene Jesús R. González Martínez$^1$, Jesús Ramiro Aragón Guajardo$^2$, Rogelio Gámez Corrales$^3$, Luis Ivan Serrano Corrales$^4$, Keren Hapuc Gutiérrez Acosta$^5$ and Anna Bertha López Oyarzá$^6$; 1Departamento de Investigación en Física, Universidad de Sonora, Hermosillo, Mexico; 2Ciencias Básicas, Instituto Tecnológico de Hermosillo, Hermosillo, Mexico; 3Departamento de Física, Universidad de Sonora, Hermosillo, Mexico; 4Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo, Mexico; 5Departamento de Matemáticas, Universidad de sonora, Hermosillo, Mexico; 6Conacyt, CICATA IPN, Altamira, Mexico.

In this paper an experimental study comparing the electrical conductivities of stabilized bilayer graphene with different organic materials is presented. To carry out this work we used a variant of the graphene synthesis method by mechanical graphite exfoliation, this method allows us to stabilize graphene with different materials, in this work we present the results of bilayer graphene stabilized with Bromide of hexadecyltrimethylammonium (CTAB), as well as with the biopolymers: xanthan gum and mezquite gum, and with the conductive polymer Polyvinylpyrrolidone (PVP). To perform the electrical conductivity tests, the Kelvin method or four-point method was used. The results presented are related to how the electrical conductivity of the graphenes varies in relation to the stabilizer, as well as in relation to the compaction pressure.

QN02.08.09

Grain Growth in Nanocrystalline MoS$_2$—An Experimental and Computational Investigation Aman Haque, Kehao Zhang, Joshua Robinson and Zahabul Islam; The Pennsylvania State University, University Park, Pennsylvania, United States.

In this present study, we investigate electron wind force driven recrystallization phenomenon in nanocrystalline Molybdenum disulfide (MoS$_2$) using in-situ Transmission Electron Microscope (TEM). We use a custom made micro electro-mechanical system (MEMS) device to bias the sample inside TEM. To investigate the effect of electron wind force as well as Joule heating on recrystallization phenomenon in MoS$_2$, we apply DC current at varying current density keeping it below the electro-migration failure limit. For low temperature (400 °C) chemical vapor deposited MoS$_2$, our electrical annealing scheme resulted in 3x decrease in electrical resistivity. Inside the TEM, we observed changes in selected area aperture diffraction (SAED) pattern at a current density of 1.0×10$^{-3}$ A/cm$^2$. This is an indication of grain growth phenomenon in MoS$_2$.

To comprehend the growth mechanism observed in TEM, we employ classical molecular dynamics (MD) simulation to investigate the underlying mechanism of grain growth using Reactive empirical bond-order (REBO) potential implemented in LAMMPS. In our present study, we build single layer polycrystalline MoS$_2$ with a grain size of 2.5nm using vonoroi-tessellation method. After building the model we checked overlapping of atoms at the grain boundaries. To incorporate both Joule heating and electron wind force effect, we conduct the experiment at different temperatures with an additional imparted electron wind force on each atoms. Grain boundaries of MoS$_2$ contains different types of ring defects such as 6|8, 5|7, 4|6, 4|8 as well as vacancy. 6|8 ring defects can be generated from 5|7 ring defects by inserting one Molybdenum (Mo) or 1 pair of Sulfur (S) atoms. On the other hand, 4|6 defects can arise from 5|7 defects by deleting one Mo or 1 pair of S atoms. In addition to this 6|8 ring defects can be healed to two perfect 6 rings and one 4 ring defects 4|6. In our present simulation, we also notice the similar ring defects recombination phenomena at the GBS of polycrystalline MoS$_2$. To investigate the defect annihilation at the grain boundaries of nanocrystalline MoS$_2$, we performed Nudged Elastic Band (NEB) simulation with 192 atoms containing 6|8, 4|6 and vacancy defects. Based on calculation, a defective sample containing these ring defects requires approximately 0.8 eV/atom additional energy to overcome the energy barrier. This additional energy could be provided during the electrical annealing of the sample in terms of Joule heating as well as imparted electron wind force. It is well-known that both electron wind force and Joule heating are concurrent phenomena during electrical annealing. Both Joule heating and electron wind force effect is beneficial for atomic/defect mobility. Due to the disorders and misorientations at the GBS, electron wind force are dominant at these defective sites and contributes pronounced scattering. In addition to the Joule heating, electron wind force could induce high atomic mobility at the GBS and annihilates defects to favor recrystallization. To investigate the effectiveness of annealing on mechanical properties we also conducted tensile testing of pre-annealed and post-annealed sample.

QN02.08.10

A Novel 2D Material—Long-Range Ferrimagnetic Order in a Two-Dimensional Supramolecular Kondo Lattice Jan Girovsky$^1$, Jan Nowokowski$^1$, Md. Ehesan Ali$^2$, Milos Baljozovic$^1$, Harald Rossmann$^1$, Thomas Nijs$^3$, Elise Aeby$^2$, Sylvia Nowokowska$^2$, Dorota Siewert$^4$, Gitika Srivastava$^1$, Christian Waeckerlin$^1$, Silvio Decurtins$^4$, Shi-Xia Liu$^5$, Peter Oppeneer$^1$, Thomas A. Jung$^6$ and Nirmalya Ballav$^7$; 1Paul Scherrer Institute, Villigen, Switzerland; 2Fondazione CRT, Pavia, Italy; 3Department of Physics, Swiss Nanoscience Institute, Univ. Basel, Basel, Switzerland; 4Institute of Nanoscience and Nanotechnology, Mohali, India; 5Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland; 6Department of Physics, University of Uppsala, Uppsala, Sweden; 7Chemistry, IISER, Pune, India.

Supramolecular assemblies of spin-bearing molecules on conducting substrates represent a rich platform to investigate the interplay of fundamental magnetic interactions and the emergence of novel properties in low-dimensional materials. Here we demonstrate the direct observation of long-range ferri-magnetic order emerging in a two-dimensional supramolecular Kondo lattice. The lattice consists of paramagnetic hexadeca-fluorinated iron phthalocyanine (FePhC) and manganese phthalocyanine (MnPc) molecules co-assembled into a checkerboard pattern on single-crystalline Au(111) substrates. Spectro-microscopy correlation experiments comprised by X-ray magnetic circular dichroism (XMCD) experiments and scanning tunneling microscopy and spectroscopy (STM/S) provide unambiguous evidence for the long range and local magnetic ordering. After magnetization at high magnetic fields (B > 6.5 T), remarkably, the remnant magnetic moments are oriented in out-of-plane direction containing significant orbital moment contributions. First-principles calculations reveal that the FePhC-MnPc antiferromagnetic nearest neighbour coupling is mediated by the Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction via the Au substrate electronic states.

Realization of long-range magnetic order in surface-supported two-dimensional systems has been challenging, mainly due to the competition between fundamental magnetic interactions such as the long-range Kondo effect and spin-stabilizing magnetic exchange interactions. The 2D ferrimagnetism in our case emerges from the high spin moment of the Fe and Mn atoms in the porphyrins, the precise 2D architecture and next nearest neighbor interactions mediated by the RKKY interaction. Our findings provide a prominent example of the supramolecular engineering of a 2D spin architecture with a weak nearest neighbor and next nearest neighbor interaction. Such systems invite for the local modification of individual spin systems e.g. by chemical ligation[2] and the investigation of the local response in the 2D array. Such novel, tunable and configurable "quantum breadboard"[3] materials allow for novel and insightful experiments directing towards their application in molecular quantum devices.


QN02.08.11

Role of Non-Covalent Interactions in Tuning Magnetic Properties of Two-Dimensional Materials Wei Ji; Renmin University of China, Beijing, China.

We theoretically show a symmetry breaking of magnetic moments in geometricaly equivalent Fe cations in Fe$_x$GeTe$_{2-x}$ few-layers using density functional theory calculations. The moments of two outermost Fe$^{2+}$ in a Fe$_x$GeTe$_2$ layer differ by 0.1 µB, which is a result of strongly inter-sub-layer coupled Fe cations. Such broken symmetry is exceptionally and
QN02.08.12
Disentangling the Oxygen and Water Vapor Effects on Optoelectronic Properties of Monolayer WS$_2$
Hanyu Zhang, Jeremy Dunklin, Obadiah Reid, Sanjini Nanayakkara, Jeffrey Blackburn and Elisa Miller; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

Monolayer transition metal dichalcogenides (TMDCs) are perturbed by the atmosphere; therefore, optoelectronic measurements may vary from day to day and lab to lab. Thus, we quantify changes to the optoelectronic properties of WS$_2$ monolayers with careful environmental control, namely inert gas, dry air, and humid nitrogen. Our WS$_2$ monolayers are prepared by chemical vapor deposition, where defects are present. To probe changes to the optoelectronic properties, we employ state-steady photoluminescence, transient absorption, and time-resolved microwave conductivity measurements to monitor the different phenomena resulting from dry air and water vapor. We determine that oxygen and water molecules have disparate impacts on the photoluminescence, exciton dynamics, and photogenerated carriers of monolayer WS$_2$. Our work disentangles the oxygen and water contributions and how these molecules passivate the WS$_2$ monolayer surface, which leads to differences in the optoelectronic properties. These effects introduced by water or oxygen molecules can be reversed and the original pristine WS$_2$ recovered. The conclusion of this work can further develop the interface charge transfer dynamics as well as photocatalysis applications of TMDCs.

QN02.08.13
Transferrable Polymeric Carbon Nitride/Nitrogen-Doped Graphene Films for Solid–State Optoelectronics
Xin Gan, Feiyu Kang and Runuo Lyu; Tsinghua University, Beijing, China.

Polymeric carbon nitride (PCN) is a stable semiconducting material with an intermediate band gap (2-3 eV), which is efficient for catalysis and optoelectronics. However, it is still a big challenge to synthesize large-area and transferrable PCN films for applications in solid state optoelectronics. In this work, by using nitrogen-doped graphene (NG) as a van der Waals epitaxial substrate, centimeter-size PCN films are synthesized via polymerization of melamine molecules. As-grown PCN/NG films can be then transferred onto other substrates (e.g. SiO$_2$/Si wafers, quartz slides, polymer substrates). Structural characterization reveals a polymerized structure of PCN films with nitrogen-containing heterocycles. By stacking PCN/NG films with graphene films, it is possible to construct a photodetector responsive to near-UV and UV illumination under ambient conditions. The responsivities of the photodetector are 0.59 mA/W and ~30 μA/W towards 365 nm lamp and 488 nm laser, respectively. Our PCN photodetectors also show fast response times (e.g., ~0.29 s to 488 nm laser illumination). Furthermore, our PCN photodetector can be fabricated on polymer substrates. As-obtained flexible photodetectors can maintain its photo-response after 100 times bending. Our results clearly demonstrate the possibility of employing large-area carbon-based semiconductors to meet the increasing demands of wearable and portable electronics.

QN02.08.14
Long Valley Relaxation Time of Free Carriers in Monolayer WSe$_2$
Siyuan Yang, Tengfei Yan and Xiaodong Cui; The University of Hong Kong, Hong Kong, Hong Kong.

Monolayer transition metal dichalcogenides (TMDCs), known as two-dimensional semiconducting materials, exhibit unique features like strong spin-orbit coupling and spin-valley locking. The exotic natures have attracted more and more research interests of new physics in TMDCs such as spintronics and valleytronics. However, a critical problem that limits the application is the relaxation time of spin and valley polarization. In this work, we use time-resolved Kerr rotation spectroscopy to probe the valley dynamics of excitons and free carriers in monolayer tungsten diselenide. Our result shows that the valley relaxation time of free carriers is found around 2 ns at 70 K, about three orders of magnitude longer than the excitons of about 2 ps, and 15 times larger than that of trions (130 ps).

QN02.08.15
Probing the Exciton k-Space Dynamics in Monolayer Tungsten Diselenides
Tengfei Yan and Siyuan Yang; The University of Hong Kong, Hong Kong, Hong Kong.

The dynamics of bright excitons in monolayer tungsten diselenides is studied, by pumping at exciton ground state and probing at higher energy, where excitonic excited states can be identified from the pump-probe spectroscopy. Remarkably, the rise time of the differential reflection signal increases significantly with the index of the excited states, which we attribute to the phase-space filling effect that probes the momentum distribution of ground state exciton. Our results reveal fast exciton momentum relaxation as a signature of the strong Coulomb interaction in 2D TMDCs.

QN02.08.16
On the Electronic Properties of 2D Transition Metal Carbides and Nitrides (MXenes)
Kanit Hantanasisirakul, James L. Hart, Yizhou Yang, Mitra Taheri, Steven J. May and Yury Gogotsi; Drexel University, Philadelphia, Pennsylvania, United States.

2D transition metal carbides, carbonitrides, and nitrides, known collectively as MXenes, have been receiving a great deal of attention in several scientific communities due to their outstanding properties such as high electrical conductivity, versatile transition metal chemistry, tuneable surface chemistry, and hydrophilicity. They have shown promise in many applications including electromagnetic interference shielding, energy storage, transparent conductors, catalysis, photothermal therapy, and photonics. To date, about 30 MXenes such as Ti$_2$C, Ti$_3$C$_2$, Ta$_2$C$_2$, Mo$_2$C, Mo$_2$TiC$_2$, Mo$_2$Ti$_3$C$_2$, Nb$_2$C, and Nb$_2$C$_2$, have been experimentally synthesized and a dozens more predicted to be stable with interesting electronic properties. In this talk, an overview of electronic properties of this large 2D materials family is presented and discussed. Transport and magnetoelectric properties of free-standing MXene films were studied by temperature-dependent resistivity measurements from 2-300 K with and without external magnetic field up to 9 Tesla. Control over MXenes' electronic properties was achieved by controlling their intercalation and surface termination via high-temperature annealing in inert atmosphere.

QN02.08.17
Control of MXenes’ Electronic Properties Through Termination and Intercalation
James L. Hart, Kanit Hantanasisirakul, Andrew Lang, Babak Anasori, David Pinto, Yevheniy Pivak, J. Tijn van Ommer, Steven J. May, Yury Gogotsi and Mitra Taheri; Drexel University, Philadelphia, Pennsylvania, United States; DENSolutions, Delft, Netherlands.

MXenes are an emerging class of 2D transition metal carbides, nitrides, and carbonitrides which show promise for applications in energy storage, electromagnetic interference shielding, and catalysis. For these applications, MXenes’ excellent performance is largely due to their high metallic conductivity, and as such there is motivation to better understand and control their electronic properties. In this talk, we will discuss how the MXene surface termination and molecular intercalation can be engineered to maximize conductivity. Specifically, we will discuss in situ annealing and electrical biasing measurements of Ti$_2$C$_2$, Ti$_3$CN, and Mo$_2$TiC$_2$ performed within the TEM. With annealing, we observe molecular de-intercalation and surface de-functionalization via in situ annealing and ex situ TGA-MS. We show that intercalants strongly influence the inter-flake MXene resistance, and that intercalation can cause macroscopic negative dR/dT for multi-flake MXene samples which display metallic (positive dR/dT) intra-flake conductivity. We also show that high temperature annealing leads to the desorption of surface termination species, and that termination loss increases the MXene conductivity. This work furthers our fundamental understanding of MXene electronic properties and provides clear guidelines for optimizing the MXene conductivity for specific applications.
Surface-enhanced Raman spectroscopy (SERS) has been widely used for the analysis of ultra-low concentration bio and chemical molecules. Moreover, the SERS signals can be amplified to 10^{15} to 10^{17} times through highly localized surface plasmonic oscillations, enabling the possibility of single molecule detection. Two major theories such as chemical and electromagnetic enhancement theories are widely accepted in order to understand the enhancement mechanisms although the exact enhancement mechanism is still under debate in the literature. Among these, the electromagnetic enhancement is the first and major contributor for the SERS enhancement, which generally originates from the magnification of the electric field by the excitation of localized surface plasmons of underlying SERS active material. The second significant chemical enhancement of SERS relies on the charge transfer between chemisorbed species and the metal surface. In order to achieve both the enhancements, we developed a reliable SERS-active substrate by gold nanoparticles (Au NPs) decorated on defect-engineered CVD graphene. It is well known that the local electric field enhancement depends on the particle size, shape and also the gap between the particles in order to get the Raman signal enhancement in SERS. To achieve the Raman signal enhancement and to control the deposition density of the Au NPs, we have used a plasma treatment strategy. Experimentally, it has been observed that Au NPs are stabilized at defect sites. In an appreciation of the above, we have performed a plasma treatment of the monolayer graphene to create the defects. Control of in-plane defects in graphene was achieved by controlling the Ar/H₂ flow rates and plasma power, and post-growth functionalization was performed using electrochemical deposition. Quantitative analysis of the defect density and nature of the interaction of Au with graphene was performed using several analytical tools. As compared to the pristine graphene, higher Au NPs density and coverage is observed for plasma modified graphene samples. The intensity ratio of the D to the G band (I_D/I_G) for graphene was 1.30. However, the I_D/I_G ratio in the case of 15-sec sample was 2.31, indicating that the plasma exposure process has altered the structure of graphene with more structural defects. After gold deposition, there is a red shift in G and 2D peaks and enhancement in I_D/I_G ratio which indicates the functionalization of graphene with Au NPs. The morphological features of plasma treated graphene samples were investigated from the STEM. STEM data shows vacancy-type defects and extended line defects, which are formed during the plasma treatment. These substrates show high SERS activity toward the Rhodamine B probe molecules. The observed enhancement in SERS might be due to the structural disorder induced generation of local defects and the strong resonant energy transfer between Au NPs and graphene. Moreover, we also observed a strong quench in the background fluorescence signal from the Au and probe molecules due to the graphene. Hence, the defect-mediated efficient gold functionalization and easy charge transfer at the graphene gold interface is expected to be suitable for biosensing and Raman imaging applications.

References
1. Surface Enhanced Raman Spectroscopy, Edited by Sebastian Schlucker, WILEY-VCH Verlag & Co. KGaA, Boschtstr. 12, 69469 Weinheim, Germany.
2. Qu Chen, Kuang He, Alex W. Robertson, Angus I. Kirkland, and Jamie H. Warner, Atomic structure and dynamics of epitaxial 2D crystalline gold on graphene at elevated temperatures, ACS Nano, 10, 10418-10427 (2016).
Two dimensional materials have shown great promise in a variety of electrochemical energy conversion and storage applications, and their further developments require an improved understanding of the atomistic mechanisms and effective design principles. I will discuss how the electronic structure of 2D materials controls atoms adsorption, and use this understanding to explain a number of puzzles, including: why structurally similar C forms/defects have distinct binding energies with Li [1], and why graphite has a low Na capacity while a high capacity for other alkaline metals [2]. This understanding also leads us to new catalysts for water splitting [3]. Finally, I will discuss the effects of varying charge and fixed potential in electrocatalysis of 2D materials [4], which are often neglected in modeling but are important for 2D materials due to their peculiar electronic structure, calling for re-evaluation of their electrocatalytic mechanisms by incorporating these effects into simulations.

Mo-S coordination number and role of V$_2$ with extended X-ray absorption fine structure (EXAFS) and density functional theory (DFT) calculation. The polymorphic transition induced through gas-solid reaction could be applied regardless of form factor and TMD type, even when the MoS$_2$ layer was incorporated into the carbon matrix. It enabled the fabrication of 1T-MoS$_2$-carbon nanofillers as HER electrolytocalyst and its superior catalytic performance is discussed.

11:15 AM QN02.09.09

Magnetic Properties of Proton Irradiated MnSiTe$_3$ Single Crystals Luis M. Martinez$^1$, Christian Saj$^1$, Adrian Cosio$^1$, Rubayn Olmos$^1$, Hector Iturriaga$^1$, Yu Liu$^2$, Cedomir Petrovic$^2$, Lin Shao$^3$ and Srinivasa Rao Singamaneni$^3$; $^1$University of Texas at El Paso, El Paso, Texas, United States; $^2$Brookhaven National Laboratory, Upton, New York, United States; $^3$Texas A&M University, College Station, Texas, United States.

In the recent past, van der Waals crystals have garnered much attention due to their unique and interesting properties, putting them in the spotlight for current and future research. This attention is due to their unique and interesting properties such as cleavability and tuneable magnetism. In this study, we explore the magnetic properties of Mn$_2$Si$_2$Te$_3$ (MST), a less-studied analog of Cr$_2$Si$_2$Te$_3$, after proton irradiation, which has been used as a tool to tune the magnetic properties of various materials. MST is a ferrimagnet below ~78 K, with its moments lying along the ab plane. Here, single crystals were grown using the self-flux method [1]. Crystals were irradiated with a 2 MeV proton beam with a fluency of 10$^{16}$ cm$^{-2}$. Magnetic measurements, as well as heat capacity (HC) measurements, were performed using a Versalab Vibrating Sample Magnetometer (VSM) with a temperature range of 50 – 350 K and a magnetic field of ±3 T. From M(T) curves, an estimated Curie temperature (T$_C$) ~74.35 K ±0.05 K [1]. From HC curves, it is apparent that there is a phase transition at ~71.67 K. After proton irradiation, a decrease in magnetization is observed from 14.01 emu/g to 11.78 emu/g in the ab plane. It is believed that proton irradiation may have caused a break in the ordering of magnetic ions, which reduces the exchange interaction in the system, thus causing the decrease in magnetization [2]. The magnetic anisotropy in the H/c direction is also reduced, setting the ab-axis as the easy axis. To corroborate these results, temperature dependent electron spin resonance (ESR) measurements have also been performed before and after proton irradiation. Additional measurements such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy are in progress to gain deeper insights.

SESSION QN02.10/QN01.11/QN03.12: Joint Session: Materials Science with Two-Dimensional Atomic Layers

Thursday Morning, April 25, 2019

PCC North, 100 Level, Room 129 A

11:30 AM *QN02.10.01/QN01.11.01/QN03.12.01

Materials Science with Two-Dimensional Atomic Layers Pulickel Ajayan; Department of Materials Science and NanoEngineering, Rice University, Houston, Texas, United States.

There has been tremendous interest in recent years to study two-dimensional (2D) atomic layers which form building blocks of many bulk layered materials. This was started by the spectacular discovery of graphene. This talk will focus on the materials science of the emerging field of 2D atomic layers of various compositions. Several aspects that include synthesis, characterization of defects, doping and manipulation will be explored with the objective of achieving functional structures with atomic layer building blocks. The concept of nanoscale engineering and the goal of creating new artificially stacked van der Waals solids and 3D constructs will be discussed through a number of examples including graphene and other 2D layer compositions. The talk will explore the emerging landscape of 2D materials systems that include hybrid compositions and multi-component 2D alloys. Some of the anticipated applications of these materials will also be discussed.

2:00 PM QN02.11.02

Antiferromagnetic van der Waals Materials TMPS3 and Its Potentials Je-Geun Park; Seoul National University, Seoul, Korea (the Republic of).

Magnetic van der Waals materials has been fast emerging as a new exciting field just over the last few years. Among one of the few known examples, TMPS3 with TM=transition metal elements have attracted significant attentions as it can exhibit the three fundamental magnetic model of Ising, XY and Heisenberg Hamiltonian depending on the TM elements. In this talk, I will demonstrate how we can use this unique magnetic property of these materials to learn of the old physics.

Reference
Surface Termination Dependent Work Function and Electronic Properties of Ti\textsubscript{2}C\textsubscript{2}T. MXene Thorsten Schultz\textsuperscript{1}, Nathan Frey\textsuperscript{2}, Kanit Hantanasirisuk\textsuperscript{1,4}, Soohyung Park\textsuperscript{1}, Steven J. May\textsuperscript{2}, Vivek B. Shenoy\textsuperscript{3}, Yury Gogotsi\textsuperscript{1,4} and Norbert Koch\textsuperscript{1}; \textsuperscript{1}Department of Physics, Humboldt University Berlin, Berlin, Germany; \textsuperscript{2}Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; \textsuperscript{3}A.J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; \textsuperscript{4}Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania, United States.

MXenes, an emerging family of 2D transition metal carbides and nitrides, have shown promise in various applications, such as energy storage, electromagnetic interference (EMI) shielding, conductive thin films, photonics, and photothermal therapy to name a few. Their metallic nature, wide range of optical absorption, and tunable surface chemistry are the key to their success in those applications. The physical properties of MXenes are known to be strongly dependent on their surface terminations. In this study we investigated the electronic properties of Ti\textsubscript{2}C\textsubscript{2}T for different surface terminations, as achieved by different annealing temperatures, with the help of photoclectron spectroscopy, inverse photoelectron spectroscopy and density functional theory calculations. We find that fluorine occupies a single adsorption site, whereas oxygen occupies at least two different adsorption sites. The band structure of Ti\textsubscript{2}C\textsubscript{2}T was measured and found to be largely in agreement with calculated band structures. We further measured the work function of Ti\textsubscript{2}C\textsubscript{2}T as a function of annealing temperature and found that it is in the range of 3.9-4.8 eV, depending on its surface composition. Comparing it to detailed DFT calculations shows that it is not simply obtained by averaging the work functions of uniformly terminated Ti\textsubscript{2}C\textsubscript{2} surfaces, but that the interplay between the different surface-terminates plays a crucial role.

Epitaxial Growth of Transition Metal Dichalcogenides—The Route to Wafer-Scale Single Crystal Monolayers Xiaotian Zhang\textsuperscript{1}, Tanushree H. Choudhury\textsuperscript{2}, Mikhail Chubarov\textsuperscript{2} and Joan M. Redwing\textsuperscript{1,4}; \textsuperscript{1}Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; \textsuperscript{2}2D Crystal Consortium, The Pennsylvania State University, University Park, Pennsylvania, United States.

Transition metal dichalcogenides (TMDs, MoS\textsubscript{2}, WS\textsubscript{2}, etc.) possess a range of intriguing optical and electronic properties at the single layer limit including direct bandgap, high exciton binding energies and valley polarization. While significant scientific advances have been achieved using TMD flakes exfoliated from bulk crystals, continued interest remains for the development of wafer-scale processes for TMD films. The synthesis of large area single crystal monolayers requires an epitaxial technique where the substrate provides a template for orientation and lateral growth of TMD domains that merge with minimal grain boundary formation. This is challenging, however, due to rotational symmetry in TMDs which gives rise to twins and anti-phase domains in coalesced films.

Our studies have focused on the epitaxial growth of binary TMD monolayers (MoS\textsubscript{2}, WS\textsubscript{2}, WS\textsubscript{2}, and MoSe\textsubscript{2}) by gas source chemical vapor deposition (CVD) using metal hexacarbonyl and hydride chalcogen precursors. A multi-step precursor modulation method was developed to independently control nucleation density and the lateral growth rate of monolayer domains on the substrate. Using this approach, atomically coalesced monolayer and few-layer TMD films were obtained on 2” sapphire substrates at growth rates on the order of ~1 monolayer/hour. In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to the sapphire with narrow X-ray full-width-at-half-maximum. Post-growth transmission electron microscopy carried out on monolayers transferred from the sapphire reveals that the films consist of micron-sized single crystal regions formed from merging of clusters of 0° and 180°oriented domains which are bounded by anti-phase grain boundaries (APBs). A significant reduction in the density of APBs was observed for WS\textsubscript{2} grown on hBN transferred onto sapphire. In this case, single atom vacancies in the hBN surface, which act as preferred sites for WS\textsubscript{2} nucleation, break the surface symmetry leading to a preferred domain orientation. WS\textsubscript{2} monolayers epitaxially grown on hBN also exhibit increased photoluminescence intensity and improved transport properties (as measured in field-effect devices) compared to comparable layers grown on c-plane sapphire. The results demonstrate hBN as a superior substrate for epitaxial growth of single crystal TMD films with a reduced density of APBs and improved properties and motivate continued efforts in the development of high quality hBN templates for wafer-scale films.

Growth and Characterization of Monolayer WS\textsubscript{2}-ferromagnet Heterostructures for Spintronics Nguyen M. Vu\textsuperscript{1}, Steve Novakov\textsuperscript{1}, Bhakti Jarwala\textsuperscript{2}, Azimkhan Kozhakhmetov\textsuperscript{2}, Joshua Robinson\textsuperscript{1} and John Heron\textsuperscript{1}; \textsuperscript{1}University of Michigan, Ann Arbor, Michigan, United States; \textsuperscript{2}Pennsylvania State University, State College, Pennsylvania, United States.

Transition metal dichalcogenide (TMD) monolayers, such as WSe\textsubscript{2}, WS\textsubscript{2}, MoSe\textsubscript{2}, and MoS\textsubscript{2}, possess distinct physical properties due to the strong coupling between spin and valley degrees of freedom.\textsuperscript{(1, 2)} As monolayer TMDs have a direct bandgap lying in visible range, they have been studied extensively by optical methods.\textsuperscript{(2, 3)} Heterostructures of monolayer TMDs with other functional materials are currently attracting significant attention due to the opportunities to access and utilize their spin-valley degrees of freedom through electrical means.\textsuperscript{(4)} For instance, TMD-ferromagnet heterostructures have been employed recently to study spin current generation in TMDs. \textsuperscript{(4, 5)} The quality of atomically thin TMDs, however, is strongly affected by deposition techniques of metallic layers and have not been fully investigated.\textsuperscript{(6)} In this work, we report the fabrication of Pt/Co multilayer using pulsed laser deposition (PLD) on monolayer WSe\textsubscript{2} grown by metalorganic chemical vapor deposition (MOCVD) on single crystalline (0001)-oriented Al\textsubscript{2}O\textsubscript{3} substrates. PLD is a plasma based deposition technique capable of tuning of kinetic and thermodynamic conditions over an expanse range to elucidate and control fundamental structure-property relationships across a wide variety of material classes.\textsuperscript{(7)} Using Raman Spectroscopy, we monitor deposition induced damage on monolayer WSe\textsubscript{2}. The pressure of Argon process gas is found to suppress deposition induced defects in WSe\textsubscript{2}, which indicates that the primary source of defect generation comes from ion bombardment. Further, we report on magnetometry and spin torque measurements of our WSe\textsubscript{2}-ferromagnet heterostructures and demonstrate the generation of spin current from TMD layer. We anticipate that our results will advance the electrical investigation of spin-valley and spin generation phenomena in 2D hybrid heterostructures for spintronics.


**4:00 PM QN02.11.07**

**Bulk Properties of van-der-Waals Hard Ferromagnet VI$_3$**

Suhan Son$^{1,2}$, Matthew J. Coak$^{1,2}$, Nahyun Lee$^1$, Jonghyeon Kim$^1$, Tae Yun Kim$^1$, Hayrullo Hamidov$^{3,4,7}$, Hwanbeom Cho$^{1,2}$, Cheng Liu$^1$, David M. Jarvis$^1$, Philip A. Brown$^1$, Jae Hoon Kim$^1$, Cheol-Hwan Park$^{1,2}$, Daniel I. Khomskii$^3$, Siddhart Saxena$^6$ and Je-Geun Park$^{1,2}$.

Center for Correlated Electron Systems, Institute for Basic Science, Seoul, Korea (the republic of); 1Physics and Astronomy, Seoul National University, Seoul, Korea (the republic of); 2Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; 3Physics, Yonsei University, Seoul, Korea (the republic of); 4Center for Theoretical Physics, Seoul National University, Seoul, Korea (the republic of); 5Navory Branch of the Academy of Sciences of Uzbekistan, Navoiry, Uzbekistan; 6National University of Science and Technology "MISIS", Moscow, Russian Federation; 7Universitat zu Koln, Koln, Germany.

We performed comprehensive measurements of the structural, magnetic and electronic properties of layered van-der-Waals ferromagnet VI$_3$ down to low temperatures. Despite belonging to a well-studied family of transition metal trihalides such as CrI$_3$, a-RuCl$_3$ and TiCl$_3$, this material has received very little attention. We outline, from high-resolution powder x-ray diffraction measurements, a corrected room-temperature crystal structure to that previously proposed and uncover a structural transition at 79 K, also seen as a peak in the heat capacity. Magnetization measurements confirm VI$_3$ to be a hard ferromagnet (9.1 kOe coercive field at 2 K) with a high degree of magnetic anisotropy, and the pressure dependence of the magnetic properties provide evidence for the two-dimensional nature of the magnetic order. Optical and electrical transport measurements show this material to be an insulator with an optical band gap of 0.67 eV - the previous theoretical predictions of d-band metallicity then lead us to believe VI$_3$ to be a correlated Mott insulator. Our latest band structure calculations support this picture and show good agreement with the experimental data. We suggest VI$_3$ to host great potential in the thriving field of low-dimensional magnetism and functional materials, together with opportunities to study and make use of low-dimensional Mott physics.

**4:15 PM QN02.11.08**

**Mobility Fluctuation Induced Linear Positive Magnetoresistance in 2D Semiconductor Bi$_2$O$_5$Se Nanoplates**

Peng Li$^1$, Ali Han$^2$, Chenhui Zhang$^2$, Xiaoxing Mao$^1$; Institute for Quantum Computing, University of Waterloo, Waterloo, Ontario, Canada; 2Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Bi$_2$O$_5$Se is a promising 2D semiconductor with ultrahigh mobility and excellent stability in ambient conditions. We report the observation of positive and linear magnetoresistance in both types of chemical vapor deposited Bi$_2$O$_5$Se nanoplates, which have different underlying mechanism. In Se rich Bi$_2$O$_5$Se samples, the transport mobility is typically smaller than 300 cm$^2$/Vs, and they show a smaller linear magnetoresistance that is proportional to the mobility. In Se poor Bi$_2$O$_5$Se nanoplates, the pronounced Shubnikov-de Hass oscillations lie in the linear magnetoresistance background. The Bi$_2$O$_5$Se nanoplates show a typical 2D conduction feature with small effective mass, i.e. 0.02m0. The average transport Hall mobility, i.e. less than 5500 cm$^2$/Vs, is significantly reduced, compared to the ultrahigh quantum mobility that is as high as 16200 cm$^2$/Vs. The spatial mobility fluctuation induced by Se vacancies between conducting (Bi$_2$O)$_2$ layers gives rise to the linear magnetoresistance, which are strongly supported by Hall transport and Shubnikov-de Hass oscillation analyses. Our finding expands the understanding of this 2D semiconductor and explores its potential magnetoresistive device application.

**4:30 PM QN02.11.09**

**Optical Phonon Coherent Oscillations in Single Layer MoS$_2$**

Chiara Trovatello$^{1,2,4}$, Henrique Miranda$^2$, Alejandro Molina-Sánchez$^3$, Luca Moretti$^2$, Rocio Borrego Varillas$^1$, Lucia Guzzer$^1$, Margherita Mauiri$^1$, Andrea Ferrari$^2$, Giancarlo Soavò$^2$, Andrea Marin$^2$, Ludger Wirtz$^2$, Giulio Cerullo$^1$, Davide Sangalli$^3$ and Stefano Dal Conte$^1$.

1Physics Department, Politecnico di Milano, Milan, Italy; 2Institute of Condensed Matter and Nanoscience (IMCN), Université Catholique de Louvain, Louvain, Belgium; 3Institute of Materials Science, University of Valencia, Valencia, Spain; 4Cambridge Graphene Center, University of Cambridge, Cambridge, United Kingdom; 5CNR-ISM, Division of Ultrafast Process in Materials (FLASHit), Monterotondo Scalo, Italy; 6Université du Luxembourg, Luxembourg, Luxembourg.

Single layer Transition Metal Dichalcogenides (1L-TMDs) are 2D direct bandgap semiconductors that have recently received significant attention for their potential suitability in photonic and optoelectronic applications. Due to the strong quantum confinement, the optical response of 1L-TMDs is strongly renormalized by excitonic effects. In the electronic bandstructure of single layer MoS$_2$ we can distinguish A, B and C excitonic peaks at 1.9eV, 2.05eV and 2.87eV, respectively.

The phonon bandstructure of single layer MoS$_2$ identifies two Raman active optical phonon branches, A$_1$ (out-of-plane) and E' (in-plane). Raman spectroscopy is extensively used to determine the number of layers in TMD samples, according to the layer-dependent frequency shift of the characteristic optical phonon frequency. Although vibrational modes of TMDs have been largely investigated by continuous wave Raman scattering, their behaviour in the time domain is almost unexplored. For instance, the generation mechanism of coherent optical phonons is still unclear. A$_1$ and E' modes have characteristic frequencies of 378cm$^{-1}$ and 406cm$^{-1}$, respectively, and the corresponding coherent oscillation period in time domain is 86 fs for the E' mode and 82 fs for the A$_1$ mode.

Here we use visible femtosecond pump-probe spectroscopy to detect impulsively excited coherent optical phonons in single layer MoS$_2$, in order to track the electron-phonon coupling across A, B and C transitions, and to understand what is the fundamental generation mechanism of coherent phonons. A frequency tunable sub-20fs pump pulse excites electron-hole pairs in the system, while a time-delayed broadband probe pulse, covering A, B and C excitonic spectral region (1.8-3.1eV), monitors the transient optical response. We find that optical phonons coherently modulate the transient optical response across all the three excitonic transitions, but predominantly across the C peak. Superimposed on the coherent electronic relaxation, we can clearly distinguish coherent oscillations, which have a period of 82fs, an amplitude of 2% of the signal peak, and a dephasing time of 2ps. The Fourier transform of this oscillating signal is peaked at the frequency of the A$_1$ mode (406cm$^{-1}$), while no signature of the coupling with the E' mode is detected.

The oscillation amplitude, i.e. electron-phonon coupling strength, which is maximum across the C peak, significantly lowers approaching B and A transitions. These observations are quantitatively supported by *ab initio* calculations computed in the framework of finite-differences of the dielectric function, also including excitonic effects. The proposed mechanisms for the generation of coherent optical phonons are Impulsive Stimulated Raman Scattering (ISRS) and Displacive Excitation of Coherent Phonons (DECP). In case of ISRS, femtosecond laser pulses impulsively activate all the Raman modes, if the laser pulse is shorter than the period of the phonon oscillation. Instead in DECP as carriers are photoexcited a sudden change in the energy potential surface acts as a kick for the generation of coherent optical phonons. Different from ISRS, DECP requires a preserved lattice symmetry, therefore only the A$_1$ mode (out-of-plane) can be excited. This strongly calls for the exclusive coupling with the A$_1$ mode and the absence of the E' mode, which is exactly what we observe.

The generation mechanism can be also deduced by the trend of the optical amplitude with the pump photon energy. As it is tuned from 2eV (A-B peaks) towards 3eV (C peak) the A$_1$ oscillations amplitude has a dramatic increase, and it lowers again for higher pump photon energies (4.3eV). *Ab initio* calculations also confirm that this trend tracks the imaginary part of the Raman susceptibility tensor, as required in DECP process.

All these observations reveal that in single layer MoS$_2$ the fundamental mechanism which is responsible for the generation of coherent optical phonons is the displacive excitation.
Neuromorphic computing systems using electronic synapses and neurons have been extensively studied in recent years due to its ability to perform analog computing for artificial intelligence. It is also expected to overcome the high energy and various limitations of today’s computing systems. Most of all analog switching device based on the two-terminal memristor, such as conductive bridging random access memory (CBRAM) and oxide based resistive random access memory (RRAM). The memristors are operated by movement of anion vacancies or forming of metal filament, which exhibit relatively good retention and endurance for neuromorphic circuits. However, since the anion vacancies or metal ions must move within the oxide by an electric field, these devices necessarily require high operating voltages of several V or more even few-nm switching oxide. The high operating voltage causes problems such as reduced overall device stability and increased device operation energy.

On the other hand, TMDC (transition metal dichalcogenide) materials have been of much attention as a kind of two dimensional (2D) material, due to its high carrier mobility and compressibility. The TMDC materials effectively block metal ion transport due to the high bonding energy and the close packing structure of atoms within the single layer. However, the metal ions can be transported through defect sites such as grain boundaries and vacancies, thus enabling the operation of the TMDC memristor. In particular, the bi-layer TMDC, in which the defect site is effectively controlled through transfer process, has the advantage of significantly improving the device-to-device uniformity and endurance. This is because the transfer process with rotation converts most of the defect sites to point defects. In contrast, the mono-layer TMDC has high possibility of line defect such as grain boundary, so that the uniformity and endurance of memristor are not secured.

Finally, we fabricated the memristors of metal / 2L-MoS\textsubscript{2} / metal structure using MOCVD technique and rotated transfer method. These devices show bipolar memristor behavior with a lower set/reset voltage of \(0.5 \text{V} \sim 0.47 \text{V}\) than the conventional oxide based memristor. The resistance changes of the device from tens of to hundreds of ohms-um\textsuperscript{-2}\ is found to occur mainly in 2D materials through external voltage measurement. It also shows the possibility of analog memory whose resistance varies linearly with bias applied from 0.3 \text{V}. Also, we confirmed STDP (spike-timing-dependent plasticity) operation in a single device, and tested various applications using a cross-bar structure. This work is an important foundation for developing devices physics to understand the memristive characteristics of 2D material-based memristor and providing neuromorphic computing systems based on such memristors.

### 9:45 AM QN03.01.02

**Synergistic Gating of Electro-Iono-Photoactive 2D Chalcogenide Neuristors—Co-Existence of Hebbian and Homeostatic Synaptic Metaplasticity**

Rohit A. John, Arindam Basu, Zheng Liu and Nripan Mathews; Nanyang Technological University, Singapore, Singapore.

Emulation of brain-like signal processing with thin-film devices could lay the foundation for building artificially intelligent learning circuitry in future. Encompassing higher functionalities into single artificial neural elements will allow the development of robust neuromorphic circuitry emulating biological adaptation mechanisms with drastically less neural elements, mitigating strict process challenges and high circuit density requirements necessary to match the computational complexity of the human brain. Here, 2D transition metal dichalcogenide (TMDC) (MoS\textsubscript{2}) neuristors are designed to mimic intracellular ion endocytosis-exocytosis dynamics / neurotransmitter-release in chemical synapses using three approaches: (i) electronic-mode: a defect modulation approach where the traps at the semiconductor-dielectric interface are perturbed, (ii) ionotronic-mode: where electronic responses are modulated via ionic gating and (iii) photoactive-mode: harnessing persistent photoconductivity or trap-assisted slow recombination mechanisms. Exploiting a novel multi-gated architecture incorporating electrical and optical biases, this incarnation not only addresses different charge-trapping probabilities to finely modulate the synaptic weights, but also amalgamates neumodulation schemes to achieve “plasticity of plasticity-meta-plasticity” via dynamic control of Hebbian spike-time dependent plasticity and homeostatic regulation. Co-existence of such multiple forms of synaptic plasticity increases the efficacy of memory storage and processing capacity of artificial neuritors, enabling design of highly efficient novel neural architectures.

### 10:00 AM BREAK
Recent Progress on 2D Monolayer Memory Devices

This work advances the down-scaling progress of memristive devices without sacrificing key performance parameters such as power consumption (< 20 nW) or applicability to lateral on-dielectric memtransistors from monolayer molybdenum disulfide (MoS2) utilising a focused helium ion beam.

Site-specific localised irradiation with the focused probe of a helium ion microscope (HIM) allows for the creation of charged defects in the MoS2 lattice, confining the damaged region to ~5 nm. The reversible drift of these locally-seeded defects in the applied electric field changes the resistance of the semiconducting channel, opening up versatile memristive functionality due to additional tuning by the field effect. The device can reliably retain its resistance ratios and SET voltages for hundreds of switching cycles at sweep frequencies of up to 2.9 V/s. High-resolution Raman and PL spectroscopy mapping has been employed to reveal the role of mobile defective sites in the switching mechanism of the device by proxy monitoring of adsorbate-enhanced luminescence.

Cryogenic charge transport studies down to 1.5 Kelvin have revealed the impact of defect drift on device operation; parametrised by large differences between the low and high resistance states in: threshold voltages, electron mobility scaling, carrier localisation lengths, Schottky barrier heights, amplitude of 1/f noise and current density saturation. In addition, an early onset metal-insulator transition occurs in the low resistance state of the memtransistor due to the high degree of reversible doping brought about by the drift of mobile n-type donors. Moreover, we demonstrate long term potentiation and depression with sharp habituation that promises rich applications in future neuromorphic architectures, as well as the ability to tune device conductance by cross-terminal stressing with perpendicular contacts.

This work advances the down-scaling progress of memristive devices without sacrificing key performance parameters such as power consumption (< 20 nW) or applicability to synaptic emulation. In addition, we push forward the understanding of resistive switching in atomically thin devices and demonstrate the utility of field-controllable dopant drift in facilitating exotic phenomena in two dimensions.

Two-dimensional layered semiconductors have recently emerged as attractive building blocks for next-generation low-power non-volatile memories. However, challenges remain in the controllable sub-micron fabrication of bipolar resistively switching circuit components from these novel materials. Here we report on the scalable experimental realisation of lateral on-dielectric memtransistors from monolayer molybdenum disulfide (MoS2) utilising a focused helium ion beam. This work advances the down-scaling progress of memristive devices without sacrificing key performance parameters such as power consumption (< 20 nW) or applicability to synaptic emulation. In addition, we push forward the understanding of resistive switching in atomically thin devices and demonstrate the utility of field-controllable dopant drift in facilitating exotic phenomena in two dimensions.

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Monolayers of 2D materials have ultrahigh mechanical strength, which enables application of very large elastic strains (e.g., ~11% for MoS2 and 25% for graphene). The ability of sustaining such large elastic strain offers unprecedented opportunities to engineer the physiochemical properties by applying mechanical strain. In this talk, I will present two examples on the effect of strain on the properties of MoS2 layer. The first example shows that elastic tensile strain reduces the bandgap of MoS2. When a gradient strain field is applied to MoS2 monolayer, the created bandgap gradient acts as an efficient funnel of photogenerated excitons that leads to enhanced photoluminescence. The second example shows that when elastic strain is applied to the sulfur vacancy on the basal planes of monolayer 2H-MoS2, the strain modifies the local electronic structure and catalytic activity.

This talk will present the latest research progress on 2D memory materials and devices, otherwise known as atomristors. In particular the talk will highlight our work on fundamental research on switching mechanisms, performance limits, and the new application of zero-power non-volatile radio-frequency (RF) switches. The fundamental understanding is enabled by in-situ scanning tunneling microscopy studies, materials characterization, and first principles modeling. The monolayer memory devices offer fast switching below 15ns, relatively high retention and the prospects of high endurance with further studies. From an application perspective, the non-volatile RF switches offer superior scalability compared phase-change memory RF switches.
Liquid exfoliation has become an important production technique to give access to large quantities of two-dimensional nanosheets in colloidal dispersion. Importantly, this is a highly versatile technique that can be applied to numerous layered materials. In this talk, recent advancements in the liquid-exfoliation and optical characterization of a range of 2D-materials will be summarized. Unifying principles among various classes of materials in both centrifugation and optical properties were identified recently. Materials under study include various commercially available TMDs, GaS, InSe, h-BN, hydrides, and more exotic candidates such as RuCl$_3$, PdSe$_2$, LaSeTe$_2$, NiPS$_3$ or even novel synthetic organic sheet stacks (2D polymers and COFs).

All materials can be exfoliated and size-selected in a similar way yielding nanosheet dispersions with well-defined changes in their lateral dimensions and thickness. This allowed us to develop a model to understand the exfoliation in high energy processes in greater depth. In brief, the "exfoliation efficiency" (defined by the combination of layer number and lateral size that can be produced) is dependent on both interlayer and intralayer interactions. In addition, similar to the effects previously observed for MoS$_2$ and WS$_2$, the optical extinction and absorbance spectra show systematic changes across all material classes. This is of great practical importance as it allows for a rapid size determination via optical spectroscopy which can be used for further optimization of the sample preparation. For example, centrifugation can be designed in such a way to enrich dispersions in monolayers without significantly changing their lateral dimensions. In addition, we show that liquid-exfoliated nanosheets and the fundamental understanding of their optical properties is an ideal foundation to track potential degradation due to reaction with water and oxygen at time and temperature dependent optical measurements of the dispersions. This in turn allows us to elaborate ways to chemically passivate defect sites and quantify the efficiency of various passivation pathways.

**3:00 PM**

**QN03.02.03**

Germanium- and Tin Chalcogenides—Growth, Heterostructure Formation, Devices, Nanoscale Light-Matter Interactions

Peter Sutter and Eli Sutter, University of Nebraska—Lincoln, Lincoln, Nebraska, United States.

Two-dimensional group IV (Ge, Sn) monochalcogenides – compound analogues of phosphorene – are of fundamental interest due to their anisotropic crystal structure and predicted characteristics such as large exciton binding energies, tunable band offsets and charge separation in heterostructures, selective valley polarization, and multiferroic order in semiconductors with bandgaps in the visible and near-infrared range. To access these predicted properties and pave the way for applications of this family of 2D semiconductors, robust approaches toward single-layer group IV chalcogenides are required. However, realizing monolayers of this class of materials has proven challenging, both by top-down (exfoliation) and bottom-up (growth) approaches.

Here, we discuss results from in-situ low-energy electron microscopy that shed light on the fundamental growth mechanisms and identify the factors that complicate the synthesis of monolayers. We have used this insight to determine avenues for growing ultrathin crystals with thickness down to a single layer, as well as few-layer heterostructures, e.g., between mono- and dichalcogenide phases involving the same metal species. The functional properties of these materials are explored through charge transport in devices, and in particular via measurements of light-matter interactions with nanometer resolution using cathodoluminescence spectroscopy in scanning transmission electron microscopy (STEM-CL). Using a tightly focused electron beam as an excitation source, STEM-CL provides spectroscopy and mapping of light emission far below the diffraction limit to address band-edge luminescence, excitonic effects, charge separation in heterostructures, and confined photonic modes in monochalcogenide mesostructures.


**3:15 PM**

**QN03.02.04**

Electromagnetic Response of Large-Area Graphene Films

Byung Hee Hong, Seoul National University, Seoul, Korea (the Republic of).

Magnetism of graphene has attracted much attention because of its combined charge and spin manipulation useful for futuristic spintronic devices. In addition, the magnetism of carbon-based materials is particularly important for lightweight actuator/sensor devices and electromagnetic wave shielding in flexible electronics. The previous studies on graphene’s magnetism were mainly focused on paramagnetism and ferromagnetism that are related to electron spins, but the diamagnetism induced by the orbital motion of two-dimensional electron gas has been studied only by theoretical approaches due to the lack of measurable amount of samples. Recent advances in large-scale synthesis of graphene enabled a facile preparation of massive graphene samples by multiple stacking and transfer. Here we report a giant orbital diamagnetism in ultra-thin, lightweight, flexible, and transparent graphene films grown by chemical vapor deposition (CVD), where the diamagnetic susceptibility in perpendicular direction is measured to be ~100 times greater than the strongest diamagnetic materials such as bismuth. As a result, the graphene film also exhibits two orders stronger electromagnetic interference (EMI) attenuation characteristics normalized to the thin film thickness than conventional EMI shielding or absorbing materials over wide frequency ranges. The EM wave induces an oscillating magnetic moment generated by the orbital motion of moving electrons, which efficiently absorbs the EM energy and dissipate it as a thermal energy. In this case, the mobility of electron is more important than the conductivity, because the EM-induced diamagnetic moment is directly proportional to the speed of electron in an orbital motion. To control the charge carrier mobility of graphene we functionalized substrates with assemblies of monolayers (SAM). As the result, we find that the graphene showing the Dirac voltage close to zero can be more efficiently heated by EM waves. In addition, the temperature gradient also depends on the number of graphene. We expect that the efficient and fast heating of graphene films by EM waves can be utilized for smart heating windows and defogging windshields.

**3:45 PM**

**QN03.02.05**

Tailoring Commensurability of hBN/Graphene Heterostructures Through Substrate Morphology and Epitaxial Growth Conditions

Daniel J. Pennachio, Chance C. Omelas-Skarin, Nathaniel S. Wilson, Elliot C. Young, Anthony P. McFadden, Tobias L. Brown-Heft, Kevin M. Daniels, Rachael L. Myers-ward, D. K. Gaskill, Charles R. Eddy and Chris Palmstrom, Materials Department, University of California, Santa Barbara, California, United States; Electrical Engineering and Computer Science, University of California, Irvine, Irvine, California, United States; Electrical and Computer Engineering, University of California, Santa Barbara, California, United States; U.S. Naval Research Laboratory, D.C., District of Columbia, United States.

Many of the intriguing properties of single-crystal 2D devices rely on the relative rotational alignment between layers. For instance, in the graphene/hBN system, substantial band structure modulation can occur at specific interlayer alignments [1], but a misalignment may be beneficial if innate graphene properties are to be examined, as in the case with near-commensurate bilayer graphene showing superconductivity [2]. To allow for scalable graphene/hBN heterostructure formation, this work investigates hBN growth on single-crystal epitaxial graphene (EG) on macroscopically aligned SIC(0001) substrates. The presented results suggest that the EG/SiC(0001) macrosteps influence hBN epitaxy such that a metastable, 30° in-plane hBN/EG rotational alignment is more favorable in certain growth regimes than the fully commensurate hBN/EG alignment, despite their similar crystal structures.

Plasma-enhanced chemical beam epitaxy (PE-CBE), an ultra-high vacuum (UHV) compatible process, was utilized to provide a clean environment for examination of the hBN structural, electrical, and chemical properties via in-situ and in-vacuo characterization methods. To determine the effect of substrate macrostep morphology, SIC(0001) substrates with a 4° offset toward <1120> and nominally on-axis substrates were used. The alignment of the hBN/EG/SiC(0001) heterostructure was studied by relating in-situ electron diffraction to nuclei edge directions found using ex-situ atomic force microscopy (AFM). Preferential alignment of the hBN nuclei edges to the SIC macrosteps was found in growths with a lower precursor flux (~1 nm/hr. growth rate), while far lower preference was found for higher-flux depositions (16 nm/hr growth rate). In addition, cross-sectional TEM confirmed the registry and rotational alignment of the hBN to the EG/SiC substrates for both growth conditions, while plan-view TEM showed a single crystal alignment.

Energy dispersive X-ray spectroscopy (EDS) during scanning TEM showed the graphene layers remained after the growth process and an atomically sharp hBN/EG interface was present. No hBN/EG intermixing between the layers was detected in either EDS or X-ray photoelectron spectroscopy (XPS). High-resolution topographic measurements and electrical measurements confirming the dielectric integrity of the hBN layer were performed using in-vacuo scanning tunneling microscopy (STM) and conducting AFM. The macrostep-directed epitaxy of hBN on EG highlighted in this work shows how different levels of commensurability can be achieved solely by tuning growth parameters during van der Waals epitaxy, thus reducing the reliance on manual rotation during film transfer and increasing the viability of scalable, single-crystal heterostructure growth.
Two-dimensional (2D) layered 3-rhombobedral (3R) phase transition metal dichalcogenides (TMDs) have received significantly increased research interest in nonlinear optical applications due to their unique crystal structures and the broken inversion symmetry. However, controlled growth of 2D 3R phase TMDs still remains a great challenge. In this work, we report a universal growth method for large area TMDs atomic layers with controllable crystal phases via a developed temperature selective physical vapor deposition route. Large area triangular 3R phase TMDs (e.g. WS\textsubscript{2} and WSe\textsubscript{2}) layers are synthesized at a lower deposition temperature. Steady state and time-resolved photoluminescence (PL) spectroscopy and Raman spectroscopy have been used to study the unique properties of 3R phase layers due to different layer stacking and interlayer coupling. Moreover, with broken inversion symmetry, 3R phase layers show a quadratically increased second harmonic generation (SHG) intensity with respect to layer numbers. Furthermore, by polarization-resolved SHG, we observe a uniform polarization preference in bilayer and trilayer 3R phase WS\textsubscript{2}, which could be a benefit for practical applications. Our results not only contribute to the controlled growth of 2D TMDs layers with different phases but also pave the way to the promising nonlinear optical devices.

4:15 PM QN03.02.07

Chemical Vapor Deposition Synthesis and Characterization of Ultra-Thin Single-Crystal Metallic Molybdenum Dioxide Nanosheets

Anup Chakraborty, Sandhya Susarla, Anand B. Puthirath and Pulickel Ajayan; Rice University, Houston, Texas, United States.

Two-dimensional materials such as graphene and transition metal dichalcogenides (TMDs) show intriguing properties compared to their bulk counterparts. Most of these materials crystallize in hexagonal systems with covalent bonding in two dimensions and weak van der Waals' bonding in the out-of-plane direction. Recently, two-dimensional transition metal oxides have attracted enormous attention due to their unique differences compared to the other chalcogenides in terms of structure, properties, and chemistry which are important for potential applications. Most syntheses so far have been achieved via exfoliation and sol-gel methods which result in good yield but lack size and quality control. In this work, we explore the synthesis of ultra-thin molybdenum dioxide (MoO\textsubscript{2}) nanosheets using chemical vapor deposition. Unlike Mo-based chalcogenides, MoO\textsubscript{2} crystallizes in a monoclinic structure with anisotropy. We achieve single-crystal flakes with lateral size of tens of microns and thickness of ~5 nm as confirmed via atomic force microscopy. The crystal structure is verified with high resolution transmission electron microscopy and grazing incidence X-ray diffraction whereas Raman, FTIR, and X-ray photoelectron spectroscopies reveal the intricate changes in the bond vibration and binding energy shifts. The flakes show strong optical absorption at ~550 nm and high metallic conductivity as verified by transport measurements. The structural anisotropy of the as-synthesized MoO\textsubscript{2} flakes was verified with polarized Raman spectra for vibration modes at 205 cm\textsuperscript{-1} and 745 cm\textsuperscript{-1}. Experiments for hydrogen evolution reaction showed catalytic properties of the as-synthesized MoO\textsubscript{2} nanoflakes at 0.4V. The mechanical properties of the flakes were investigated with nanoindentation and nanoscratch experiments. The work shows a facile way of synthesizing metallic nanosheets with potential optoelectronic, catalytic, and mechanical applications.

4:30 PM QN03.02.08

Oligothiophene-Bridged Conjugated Covalent Organic Frameworks

Niklas Keller, Derya Bessinger, Stephan Reuter, Mona Calik, Laura Ascherl, Fabian Hanusch, Florian Aurual and Thomas Bein; LMU Munich, Munich, Germany; University of Cambridge, Cambridge, United Kingdom.

2-Dimensional covalent organic frameworks (2D-COFs) are crystalline porous materials comprising aligned columns of π-stacked building blocks. Regarding potential applications of COFs in organic electronics and optoelectronics, access to oligothiophene-based COFs would be of great interest. However, the realization of such materials has remained a challenge, in particular concerning the laterally conjugated imine-linked COFs. We have developed a new building block design, implementing an asymmetric modification on an otherwise symmetric backbone that allows us to obtain a set of highly crystalline quaterthiophene (4T)-derived COFs with tunable electronic properties. Studying the optical response of these materials, we have observed for the first time the formation of a charge transfer state between the COF subunits across the imine bond.

In this work, we have developed the first quaterthiophene-based 2D covalent organic frameworks comprising ordered π-stacked columns of 4T and pyrene moieties. Applying an asymmetric functionalization strategy of the otherwise C2-symmetric 4T backbone allowed us to incorporate alkyl chains for optimized solubility while still retaining the ability of the building blocks to stack in close-packed face-on thiophene columns. We also demonstrate that this approach provides a facile route for modifying the electronic properties of the 4T backbone via incorporation of electron-deficient subunits, thus forming donor-acceptor type chromophores. The absorption and emission spectra confirm that the 4T-based building blocks are electronically integrated into the framework. Spectral features below the energy of the π-π* transition and the analysis of the corresponding emission decay time traces reveal the fast and efficient formation of a charge transfer state between the imine-linked pyrene and quaterthiophene subunits. We believe that our new asymmetric building block design provides a general strategy for the synthesis of well-ordered COFs from various extended building blocks. This will greatly expand the range of applicable molecules for realizing frameworks with tailor-made optoelectronic properties.


4:45 PM QN03.02.09

Bottom-Up Synthesis of Ultrathin PdSe\textsubscript{2} Crystals with High Electron Mobility

Yixi Qin\textsuperscript{1, 2, 4}, Yiling Yu\textsuperscript{1}, Chenze Liu\textsuperscript{1}, Hui Cai\textsuperscript{2}, Akino Odo\textsuperscript{2}, Anna N. Hoffman\textsuperscript{1}, Yu-Chuan Lin\textsuperscript{1}, Alexander A. Puretzky\textsuperscript{2}, Gerd Duscher\textsuperscript{2}, Philip D. Rack\textsuperscript{1, 2}, Christopher M. Rouleau\textsuperscript{1}, David B. Geonhgan\textsuperscript{1} and Kai Xiao\textsuperscript{1}; Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China; Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; Department of Materials Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States; University of Chinese Academy of Sciences, Beijing, China.

PdSe\textsubscript{2} is a high-mobility 2D material that has an unusual pentagonal structure, leading to buckled and puckered layers. Its strong interlayer coupling results in highly interesting and asymmetric optoelectronic properties and makes it difficult to exfoliate. However, to date it has not been directly synthesized on substrates. In this work, we report the bottom-up, vapor transport growth of few-layer PdSe\textsubscript{2} crystals that are rectangular and tens of microns in size. The high quality of the PdSe\textsubscript{2} crystals were confirmed by low-frequency Raman spectroscopy, atomic force microscopy (AFM), and high resolution annular dark field scanning transmission electron microscopy (ADF-STEM). Second-harmonic generation (SHG) mapping analysis of the PdSe\textsubscript{2} flakes was used to characterize their strong optical anisotropy. Field-effect transistors made from the few-layer PdSe\textsubscript{2} crystals revealed tunable ambipolar charge carrier conduction with a high electron mobility of ~78 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, which is comparable to that of exfoliated PdSe\textsubscript{2}, indicating the promise of this anisotropic 2D material for electronics.

Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterized were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.
The continuous miniaturization of electronic devices has propelled modern technologies to higher performance and efficiency, but future progress requires a shift from traditional semiconductors towards new multifunctional systems and integration technologies. The development of two-dimensional (2D) van der Waals (vdW) crystals has led to the discovery of new phenomena and the realization of several functional devices. Among these vdW crystals, the metal chalcogenide InSe compound represents a promising semiconductor [1-6]. Our recent demonstration of fast broad-band photodiodes [1], field effect transistors (FETs) with electron mobility higher than in Si-FETs [3], and quantum devices [4, 6] has revealed the great potential of this material. From the growth and fundamental studies to the demonstration of prototype devices, this talk will describe how these systems can provide a platform for scientific investigations and new routes to 2D electronics and optoelectronics.

References

11:00 AM QN03.03.02
Hexagonal Boron Nitride as a Buffer Layer in Monolayer Molybdenum Disulfide Transistors

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One current problem with the fabrication of devices using two-dimensional (2D) materials as the semiconducting channel is the formation of a high-quality semiconductor-dielectric interface. Seeding for atomic layer deposition (ALD) films is notoriously difficult on van der Waals (vdW) layers due to the absence of dangling bonds. One method to improve the seeding on vdW materials is to use plasma-enhanced atomic layer deposition (PEALD). However, PEALD often damages the top-most layers which prevents the use of PEALD on monolayer materials.

Here we investigate the use of few-layer hexagonal boron nitride (h-BN) as an interfacial buffer layer transferred on top of monolayer molybdenum disulfide (MoS2) before deposition of the top dielectric. Top-gated monolayer MoS2 transistors with various dielectric stacks are fabricated and the h-BN layers’ impact is characterized via optical and electrical measurements.

11:15 AM QN03.03.03
What Limits the Intrinsic Carrier Mobility of Two-Dimensional Metal Dichalcogenides?

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Two-dimensional (2D) metal dichalcogenides (MX2) are the most common type of 2D semiconductors and have shown great potential for a wide range of chemical and physical applications. However, they are limited by a low electron/hole mobility, which has been recognized as one of the major challenges impeding their further developments, and urges efforts to understand the mobility-limiting factors and discovery of higher-mobility alternatives. Here using density functional perturbation theory and Wannier interpolation of the electron-phonon matrix to study a wide range of MX2, we find that the intrinsic carrier mobility, in contrast to common belief, neither correlates with the effective mass nor can be assessed by the widely used deformation potential theory; instead it is limited by the longitudinal optical (LO) phonon scattering for most MX2, while for MoS2 and WS2, the mobility is limited by the longitudinal acoustic (LA) phonon scattering. Furthermore, we find that the LO scattering strength is strongly correlated with the magnitude of the Born effective charge, suggesting that the carrier transport is greatly affected by the electric polarization change induced by the atomic vibration. This finding enables us to use the Born effective charge to rapidly screen the 2D MX2 database for high-mobility semiconductor candidates. Our work reveals the underlying factors governing the intrinsic carrier mobility of 2D MX2, and offers a practical descriptor for discovering high-mobility candidates.

Ref: L. Cheng, Y. Liu, JACS, 2018, DOI: 10.1021/jacs.8b07871
Enhancement and Control of Circularly Polarized Emission in Monolayer Heterogeneous WS$_2$ with a Plasmonic Chiral Metasurface Wei-Hsiang Lin$^1$, Pin Chieh Wu$^1$, George. R. Rossman$^2$, Na-Chang Yeh$^3$ and Harry Atwater$^4$; 1Department of Applied Physics, California Institute of Technology, Pasadena, California, United States; 2Department of Physics, California Institute of Technology, Pasadena, California, United States; 3Division of Geological and Planetary Science, California Institute of Technology, Pasadena, California, United States.

Controlling the circular polarization of light is a key aspect for the development of functional nanophotonics for emerging applications. Monolayer transition metal dichalcogenides (TMDCs) are excellent candidates for spintronic, valleytronic and optoelectronic devices because the two inequivalent valleys in the Brillouin zone can give rise to valley-polarized photoluminescence (PL) under excitation with circular polarized light (CPL). However, the atomic monolayer thickness is a significant challenge for WS$_2$ photoluminescence emission due to its weak light-matter interaction. We investigated the feasibility of enhancing the light-matter interaction in monolayer WS$_2$ by means of the exciton-plasmon interaction with spin-orbit coupling of light. This objective was achieved by designing and fabricating plasmonic spiral rings with subwavelength dimensions on a hybrid substrate for WS$_2$, and by synthesizing high-quality WS$_2$. Specifically, we developed controlled growth of heterogeneous domains in CVD-grown monolayer WS$_2$ single crystal on SiO$_2$/Si substrate using tungsten oxide and sulfur precursors at T=850 degree C. Spatially resolved PL, Raman, X-ray photoelectron spectroscopy and Kevin probe force microscopy images revealed the formation of homojunctions in these single crystals which imply a direct correlation between the chemical stoichiometry and optoelectroheterostructure. The WS$_2$ were integrated with a plasmonic spiral ring metasurface with subwavelength sized elements, designed to enhance the light-matter interaction. Our plasmonic chiral metasurface consisted of a gold back reflector, a 20-nm-thick SiO$_2$ dielectric layer followed by a monolayer heterogeneous WS$_2$ layer on which we fabricated a gold spiral array. By optically pumping the plasmonic chiral metasurface/WS$_2$ heterostructure with CPL and measuring the resulting spatially resolved PL emission (P$_{CPL}$) at room temperature and low temperature (80K), we found the optical chirality of WS$_2$ was enhanced by more than 10 times relative to WS$_2$ layers. Additionally, by proper designs of the dimensions of the chiral metasurface structure, a linearly-polarized incident light can be converted to circularly-polarized light. These results suggest a new pathway of manipulating the valley-polarized PL emission in 2D materials via plasmonic chiral metasurfaces, which may be further applied to the development of valley-polariton optoelectronic devices.

1:45 PM QN03.05.02
Photoluminescence Enhancement at Heterojunction in WS$_2$-MoS$_2$ Lateral Heterostructures Revealed by Tip Enhanced Optical Spectroscopy Andrey Krayev$^1$, Sourav Garg$^2$, Seongsin M. Kim$^3$ and Patrick Kung$^2$; 1Horiba Scientific, Novato, California, United States; 2The University of Alabama, Tuscaloosa, Alabama, United States.

2D semiconductors such as transition metal dichalcogenides (TMDCs) recently attracted significant attention of the research community due to large number of fascinating optoelectronic and photocatalytic properties of these materials originating from their 2D nature. Defect engineering in these materials and defect-bound excitons are of particular importance due to their potential use as qubits for quantum computing. Lateral heterostructures of different TMDCs is one of possible ways of creating controlled defects. Tip enhanced optical spectroscopy (TEOS) which encompasses tip enhanced Raman scattering (TERS) and tip enhanced photoluminescence (TEPL) is a fast developing method that allows spectroscopic characterization of 2D materials with nanoscale spatial resolution and cross-correlation of this optical information with various properties revealed by scanning probe microscopy. Here we report observation of strongly enhanced PL from WS$_2$ at the grain boundary in CVD-grown monolayer of WS$_2$–MoS$_2$ lateral heterostructures transferred onto gold. Scanning Kelvin probe microscopy revealed strongly profiled saw-tooth-like junction between the MoS$_2$ and WS$_2$ sub-crystals with typical size of the features being from few hundreds to over 1000 nm. TEPL measurements showed that PL peak corresponding to WS$_2$ gets strongly enhanced within approximately 100nm next to the heterojunction. TERS spectra suggested alloying within few tens of nanometers away from formal boundary between MoS$_2$ and WS$_2$. We argue that observed strongly localized nanoscale enhancement of the WS$_2$ PL is associated with defects located at heterojunction and subsequently exciplexes bound to these defects. We’ll discuss prospective use of such structures as single photon emitters with prospective application as qubits for quantum computing.

2:00 PM QN03.05.03
Optically Active Defects in Tunable 2D Materials A.W. Holleitner; Technical University-Munich, Garching, Germany.

Atomically thin two-dimensional layered materials receive great interest because of their unique physical properties. Particularly, monolayers of semiconducting transition metal dichalcogenides, such as MoS$_2$, excel due to their strong light-matter interaction that is dominated by exciton phenomena [1-3]. Key to the integration of monolayer 2D materials into atomistic circuits is the possibility to tune and engineer their properties on demand and on-chip e.g. by defects, dielectric environment and local doping [4-8]. We will introduce a methodology based on silicon ion microscopy (SIM) to controllably realize single optically active emission centers in MoS$_2$, which show clear indications of quantum dot-like behavior. Our results demonstrate the potential of optically controlled ion beams to engineer the optical properties of semiconducting 2D materials at the nanometer scale [5,9].

We thank J. Klein, A. Kue, F. Siggter, F. Merbler, J. Wierzbowski, M. Altzschner, F. Kneipl, K. Muller, M. Kaniber, M. Florian, M. Lorke, M. Knap, R. Schmidt, J.J. Finley, and U. Wurstbauer for a fruitful collaboration and the DFG via NIM, eConversion, and project HO3324/9-1 for financial support.

References

2:30 PM BREAK

3:00 PM QN03.05.04
Emerging photoluminescence from MoS$_{2(1-x)}$Se$_x$, MoS$_2$-MoSe$_2$ and MoS$_x$-WS$_x$: Layered Semiconductor Atomic Layered Materials Ravi K. Birje$^1$, Rahul Sharma$^2$, Krishna R. Sahoo$^3$, Balakrishna Annathoju$^4$, Tharangattu N. Narayanan$^5$, Robert Dyef$^6$ and Wolfgang Theis$^7$; 1Nanoscience Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, United Kingdom; 2Tata Institute of Fundamental Research, Hyderabad, India; 3School of Chemistry, National Graphene Institute, University of Manchester, Manchester, United Kingdom.

Two dimensional (2D) layer semiconductor atomic layered materials, such as transition metal dichalcogenides (MX$_2$, where M= Mo, W, and X=S, Se, Te) and their heterostructures have attracted considerable interest. Heterostructures with atomically sharp interfaces and alloyed versions of these exhibit widely tunable band gaps as a function of composition and stacking sequence. In the present work, we demonstrate the direct physical vapour deposition (PVD) growth of MoS$_{2(1-x)}$Se$_x$, MoS$_2$-MoSe$_2$ and MoS$_x$-WS$_x$: van der Waals (vdW) heterostructures using individual TM and chalcogen precursors (MoO$_3$, WO$_3$, S and Se powders) and their enhanced optical properties in the visible light. The morphology of as-grown MoS$_2$-MoSe$_2$ and MoS$_2$-WS$_x$; and MoS$_{2(1-x)}$Se$_x$:vdW heterostructures on Si/SiO$_2$ substrates evolves from triangular to hexagonal domain shapes with decreasing coverage. It is found that the domain size in MoS$_{2(1-x)}$Se$_x$:few-monolayer alloys is larger than for MoS$_2$-MoSe$_2$, MoS$_2$-WS$_x$. The crystallinity of the atomic layers and Se composition in MoS$_{2(1-x)}$Se$_x$:MoS$_2$-MoSe$_2$ and MoS$_{2(1-x)}$Se$_x$:MoS$_2$-WS$_x$: are determined by micro-Raman spectroscopy (µRaman) and XPS, respectively. In the present case, Se composition in the MoS$_{2(1-x)}$Se$_x$: is found to be around 40:60 (i.e x=0.41, MoS$_{2(1-x)}$Se$_{0.41}$) from XPS analysis, which is consistent with the previous reports. Interestingly, we found the tunable photoluminescence fromMoS$_2$-MoSe$_2$, MoS$_2$-WS$_x$: and MoS$_{2(1-x)}$Se$_x$:in-correlation with density functional theory (DFT) calculations of modified band structure and bandgap in these monolayer heterostructures as a function of Se to S atomic percentage. Thus establishing that these few-monolayer structures are excellent candidates for optoelectronics and visible light photocatalysis applications which cover a large window of the visible wavelength.

References:
Light Emitting Optoelectronic Devices Based on van der Waals Heterostructures

Two-dimensional (2D) materials are promising due to unique optical and electrical properties. New physics observed only in 2D materials allow for development of new-concept devices by using their valleys, tunneling effect, engineered band offset, and strong light-matter interaction. Recently, van der Waals heterostructures (vdWH) have been achieved by putting these 2D materials onto another, in the similar way to build Lego blocks. Assembled 2D blocks provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional optoelectronic devices. In this talk, I introduce our recent achievement in optoelectronic devices based on van der Waals heterostructures. By engineering band alignment of the stacked 2D materials and utilizing work function tunability of graphene, light emitting devices with exceptional multi-functions were fabricated. The electrically tunable light emitting transistors and tunnel devices can emit a strong light with modulation of charge (or trion) density. So, wavelength and intensity of emitted light can be controlled by electric field. Further, light emission from interlayer exciton generated in the stacked 2D semiconductors was demonstrated in device operation for the first time. Our work shows a great promise of van der Waals heterostructures for optoelectronic applications. I will also introduce our recent progress in high integration of graphene devices (or graphene leads). We developed a novel patterning technique by using XeF2 gas and fluorographene via contacts for graphene interconnects embedded in a van der Waals heterostructure. Our via contacts can be useful for 3D integration of 2D devices for future 2D electronics.

High Photoresponsivity Ultrathin Lateral Stacking WS2—Graphene Photodetectors Made by Direct CVD Growth

Graphene is an ideal material for optoelectronic applications. Its photonic properties give several advantages and complementarities over Si photonics. I will show that graphene-based integrated photonics could enable ultrahigh spatial bandwidth density, low power consumption for next generation datacom and telecom applications. Heterostructures based on layers of atomic crystals have a number of properties often unique and very different from those of their individual constituents and of their three dimensional counterparts. I will show how these can be exploited in novel light emitting devices, such as single photon emitters, and tunable light emitting diodes.

High Photoreponsivity Ultrathin Lateral Stacking WS2—Graphene Photodetectors Made by Direct CVD Growth

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Two dimensional transitional metal dichalcogenides (TMDs) have been widely investigated in recent years for their electronic, optical and catalytic properties as well as specific mechanical properties. In addition, the characteristics of TMDs would be determined by the layer numbers or layer stacking configurations. Thus, it is essential to design a method for developing new 2D-architecture by tailoring the properties of the material. In this work, we provided a sub 10nm localized thinning technique of atomic layers WS	extsubscript{2} via in-situ scanning transmission electron microscopy (STEM/TEM). The entire process was visualized at atomic scale and conducted at high temperature. In the beginning, we shortly presented a methodical CVD system to synthesize the crystalline atomic-layers WS	extsubscript{2}, followed by transferring the as-grown samples onto specialized TEM chips. Subsequently, evidenced by the TEM results, we successfully shaped the WS	extsubscript{2} layer by partially peeled off each WS	extsubscript{2} monolayer. Additionally, during the thinning process, the exclusive 2D-behaviors such as nanolayers migration, coalescence and etching were observed. Finally, we utilized atomic resolution STEM images to identify layer variation and structural configuration, which helped us deduce the exact atomic stacking sequence. Further EDS/EELS analysis provide elemental information to elucidate the sulfur depletion mechanism. This sculpting technique allows for sub-10nm thinning features while preserving the crystallinity, and also paves the way for the rational design of WS	extsubscript{2}-based quantum and optoelectronic devices.

**QN03.06.02**
Solution Processed Transition Metal Dichalcogenides for Printed Electronics Applications

Joe Neilson; The University of Manchester, Manchester, United Kingdom.

Semiconducting 2D materials, such as the Transition Metal Dichalcogenides (TMDs), have been widely explored for use in the fabrication of devices such as: field-effect transistors (FETs), sensors, and light emission devices, due to their attractive and size tuneable electrical properties. In particular, FETs manufactured around single mechanically exfoliated flakes with mobilities greater than 700 cm	extsuperscript{2}/V·s	extsuperscript{-1} have been widely reported. TMDs can also be handled as liquid phase dispersions, enabling the formulation of inks for use in high throughput and low cost printed electronic devices. Liquid dispersions of TMDs therefore represent an attractive alternative to current organic semiconductor technology, as mobility and on/off ratio enhancements may be possible.

However, current literature demonstrates that FETs manufactured using solution processed TMDs suffer from low mobilities and on/off current ratios. The reason for the observed shortcomings in such devices is unknown, but possible reasons can be broadly narrowed down to contamination/oxidation of the flakes, surface defects, or poor flame-flake contacts within a film of solution processed TMD material.

Here, we will present results which elucidate possible mechanisms for the poor electronic performance of solution processed TMD thin film devices. First, we have developed new methods of thin film assembly from solution processed few layer 2D material dispersions including; liquid/liquid interfacial assembly, and Langmuir-Blodgett assembly via a Pickering emulsion intermediate phase. This has resulted in average film thicknesses of less than 5 nm. Subsequently, photo and field-effect transistors were assembled around the resultant thin films. Considerable improvements to the electrical properties were achieved by the application of dielectric polymer passivation layers and careful separation of monolayer enriched material from the liquid dispersions. Alternate exfoliation routes such as chemical and electrochemical exfoliation and the effects on resulting thin film transistors have also been explored.

Revealed herein are examples of FET devices manufactured around thin films of TMDs assembled utilising various simple, low cost, and highly scalable assembly methods. This work provides insights into the manufacturability of solution processed 2D FETs by elucidating and resolving some of the failure modes associated with solution processing methods. Finally, a robust and simple all-solution processed manufacture technique for high performance thin film devices made from dispersions of 2D TMD material is demonstrated.

**QN03.06.03**
Deterministic Folding of 2D Materials for Electronic Device Applications

Huan Zhao, Beiwei Wang, Xiaodong Yan, Haozhe Wang, Jing Kong, Aiichiro Nakano, Rajiv Kalia and Han Wang; 1Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California, United States; 2Collaboratory for Advanced Computing and Simulations, University of Southern California, Los Angeles, California, United States; 3Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Atomically-thin two dimensional (2D) layered materials have exceptional mechanical flexibility. Therefore, 2D nano-sheets can be strained, stretched and folded into various origami structures and superlattices. 2D material origami structures possess unprecedented physical properties emerged from the folded edge, the interface, and the rotational angle of crystal lattices induced by the highly controllable folding direction.

In this talk, we will introduce a deterministic folding technique for creating controllable 2D material origami structures. This technique allows us to accurately fold a 2D atomic sheet at any position and direction pre-defined by standard electron beam lithography. 2D origami structures of layer-by-layer stacked heterostructure of 2D materials and large-scale CVD monolayer array will be demonstrated as examples of the scalability and controllability of this technique. We also looked deep into the molecular-level dynamics to understand the fundamental interactions underlying the folding process. Through simulation, we found the free energy of graphene increased after folding while the entropy of graphene decreased.

In addition, we will demonstrate various applications of our origami technique. 2D superlattice with controlled rotational angle can be prepared using the folding approach, which can be a powerful platform for exploring a rich array of physical phenomenon. For example, we found a pronounced Raman enhancement in a twisted graphene sample prepared by folding, suggesting the existence of Van Hove singularities. In addition, we were able to reconfigure the functionalities of 2D material electronics through folding. I will introduce a novel flash memory device built with this approach.

In summary, we developed a technique to deterministically fold 2D materials. Not only can this technique serve as a platform for studying nano-mechanics and exploring emerging physical phenomenon, but also it could be promising for realizing foldable and adaptive electronics, nano-actuating, and bio-nano interfaces.

Acknowledgment: This work is supported by the AFOSR FATE MURI program (Grant no. FA9550-15-1-0514).

**QN03.06.04**
Graphene–Si–Graphene Bipolar Junction Transistor with Tunable Gain

Ze Liu, Wenzhe Wang, Jie Huang, Audrey Rose M. Gutierrez and Zhaozhi Zhong; University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Traditional silicon bipolar junction transistor (BJT) is widely used in current amplification and high power circuits. With its compatibility to planar process, BJTs with different parameters such as doping level and base width are dedicatedly designed and fabricated to achieve large desired gains. For traditional silicon BJT, gain is determined intrinsically by the base width. The gain can be tuned by the doping concentration of the emitter, but this is a limited approach, as the doping concentration is usually limited by the maximum sheet carrier density in the emitter. For graphene, this constraint does not exist, and the gain can be tuned by the doping or the Fermi level of the emitter graphene.

Graphene–Si–Graphene BJT can also be readily applied to other type of two dimensional material–Si hybrid devices for better control and performance.

**QN03.06.05**
2D Materials as Emerging Sensing Platforms

Raman Singh, 1CSIR-CSIO, Chandigarh, India; 2AcSIR-CSIO, Chandigarh, India.

It is believed that 2 D materials have evolved from astonishing properties of graphene and are in spotlight date back to 2004 when techniques of exfoliation of graphene were discovered. Since then both layered and non-layered 2D materials have gained momentum due to their some eye catchy properties which are ascribed to the dimensionality effect
and modulation in their band structure. In recent years, these 2D materials have been used for various emerging applications viz catalysis, opto-electronic devices for sensing, high performance electrodes and nanocomposites.

Among various 2D materials, atomically layered transition metal dichalcogenides (TMDs) have been used as promising two-dimensional materials for their wide applications. Their properties like an intrinsic band gap varying with the number of layers, a direct band gap and strong spin-orbit coupling in monolayers, have attributed to their immense consideration by researchers for varied applications.

In our research, nanoscaled layered transition metal dichalcogenides have been synthesized using simple synthesis method and are used as platform for fabrication of immunosensor for diagnostic applications.

**QN03.06.06**

**An Investigation of Carrier Mobility in MoS2 Grown by Chemical Vapour Deposition in a 300nm reactor**

Emma Coleman,1 Paul Hurley,1 Scott Monaghan,1 Jun Lin,1 Farzam Gity,1 Michael Schmidt,1 James Connolly1, Lee Walsh,1 Karim Cherkaoui1, Katie O Neill1, Niall McEvoy2,Corneac OColleain2, Colm O'Dwyer3, Georg Duesberg4 and Ian M. Povey1

1Tyndall National Institute, Ballincollig, Ireland; 2CRANN, Trinity College Dublin, Dublin, Ireland; 3Chemistry, University College Cork, Cork, Ireland; 4Universität der Bundeswehr München, Munich, Germany.

Two dimensional (2D) van der Waals materials bonded exhibit a range of electronic properties spanning from semi-metals through to wide bandgap semiconductors. Potential applications include electronics, sensors and display technologies [1]. In relation to practical device applications, research is focused on large area growth [2 – 6], stable approaches to doping and contacting [7,8]. We report on the optical properties and carrier mobility in thin films (2-10nm) of MoS2 grown in a commercial 300nm atomic layer deposition reactor. The MoS2 films are grown on sapphire and SiO2/Si substrates at temperatures in the range of 350°C to 550°C by a chemical vapour deposition process using Mo(CO)6 and H2S precursors.

Analysis of the films with Raman, X-ray photoelectron spectroscopy and electron backscattered diffraction all confirm the films as MoS2. The carrier concentration, carrier type and carrier mobility are studied with Hall measurements. Excellent ohmic behaviour is achieved on MoS2 (10nm, 550°C with no post growth annealing) deposited on sapphire and a-Al2O3/sapphire substrates. Room temperature Hall analysis of the MoS2 films indicates that the non-intentionally doped MoS2 films are n-type with very low carrier concentrations of ~10^4cm^-3. Comparison of the free carrier concentrations in the grown films (~10^4cm^-3) to Hall analysis of natural and synthetic MoS2 crystals (1x10^6 to 1x10^7 cm^-3) [9], with the presence of electrically active defect states in the energy gap of the MoS2 for the polycrystalline CVD grown films [10]. MoS2 films grown at 550°C and subsequently annealed at 550°C in a H2/Ar ambient indicate a significant increase in the electron concentration (~8x10^5 cm^-3).

The electron mobility is in the range of 3 to 17 cm^2/Vs for films grown at 550°C (with comparable values for MoS2 films grown at 350°C and subsequently annealed at 550°C in a H2/SiH4). Electron mobility values up to ~17 cm^2/Vs for a MoS2 grain size in the 5nm to 20nm range in this work, compared to values in the range of 25 to 30 cm^2/Vs reported by K. Kang et al. [3] for monolayer MoS2 with a grain size around 1μm [11]. This motivates the need to investigate scattering mechanisms and the influence of grain size on electron mobility in CVD grown MoS2 and preliminary results will be shown on the temperature dependence of electron concentration and electron mobility in the CVD grown MoS2 films.

References


**QN03.06.07**

**Self-Limiting Growth of High-Quality 2D Monolayer MoS2 by Direct Sulfurization Using Precursor-Soluble Substrates**

Yang Lu and Jamie Warner; University of Oxford, Oxford, United Kingdom.

Monolayer transition metal dichalcogenides (TMDCs) have demonstrated great potential in next-generation electronics due to their unique optical and electronic properties. Considerable efforts have been made to achieve large-scale synthesis of high-quality TMDC monolayers. However, it remains challenging to produce uniform high-quality monolayer TMDCs over large scale. Vapor phase deposition methods have been known to produce high quality TMDCs suitable for large-scale device fabrication, but the nucleation and growth of 2D crystals is significantly affected by the gas flow and the geometric effect of chamber in these systems. Direct sulfurization method holds great promise in achieving large-scale synthesis, but the obtained materials suffer from small grain size and multilayer regions.

In this work, low-cost glass substrate is used to address the issues in direct sulfurization method. The synthesized monolayer MoS2 single crystals possess the largest average crystal size (~100 μm) ever reported for MoS2 grown by direct sulfurization method, with large-area uniformity which is only limited by the size of the substrate. We confirm that the ability of glass to incorporate pre-deposited precursors into its molten state is the key to the facile production of high-quality monolayer MoS2 crystals. A combination of low-cost, uniformity, scalability, simplicity and high quality is achieved in our method which showed great promise for the development of wafer scale electronic devices based on 2D materials. Our work also provides a new look at the role substrates could play in the synthesis and the possibilities of using other glass or liquid substrates for the growth of high-quality 2D materials.

**QN03.06.08**

**Tunable Plasmons in Few-Layer Graphene Anti-Dot Lattices**

Kaci L. Kuntz, Elena R. Kovalik and Scott Warren; University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

The low carrier concentration (n ~ 10^13 cm^-3) and linear band dispersion at the fermi energy E_F of graphene enable tunable optoelectronic responses with small changes in the carrier concentration, demonstrating shifts of the plasma frequency in the THz (*Nat. Nanotech.*, 6 (2011), 630-634) and mid-infrared (ACS Nano, 7 (2013), 2388-2395) regions. However, there have been limited observations of plasma shifts in the near infrared (NIR) and visible spectra, which would enable opportunities for graphene-based plasmonic sensors with high sensitivity to local dielectric environments (*Analyst*, 140 (2015), 386–406), optical tunability for fast telecommunications (*ACS Photonics*, 1 (2014), 135–152), and photovoltaics with reduced dimensions (*Nat. Mater.*, 9 (2010), 205–213). Most commonly, graphene plasmons have been tuned by (1) altering the carrier concentration through electrostatic doping (*Nature*, 471 (2011), 617–620) or (2) reducing the dimensions (*ACS Photonics*, 1 (2014), 135–152). Through electrostatic techniques, the E_F can be shifted as much as in eV (*Nature*, 471 (2011), 617–620); therefore, the plasmonic response of doped-graphene has been limited by the placement of the charge carriers attainable within the Dirac cone in the band structure, where interband transitions are minimized (e.g. THz and mid-IR). The second approach is reducing dimensions, demonstrated in dot (*ACS Nano*, 7 (2013), 2388–2395), ring (*ACS Nano*, 7 (2013), 2388–2395), ribbon (Nat. Nanotech., 6 (2011), 630-634), and tapered (Nature, 487 (2012), 77–91) structures; these have enabled graphene plasmons to be shifted to the mid-IR, as low as 3.7 μm (ACS Nano, 7 (2013), 2388–2395). Although graphene plasmons are generally studied in arrays, there is limited research in anti-dot (e.g. hole or nanomesh) lattices (Nano Lett., 13 (2013), 2541–2547). Here, through simulations, we investigate hexagonal anti-dot lattices, where electrostatic doping and structure parameters (i.e. radius, periodicity, number of layers) can tune the plasma frequency. We employ a finite-difference time-domain suite (FDTD Solutions in Lumerical, Inc.) to simulate the optical properties of anti-dot structures with diameter D, periodicity P, one to six layers, and bias doping up to 0.8 eV. The graphene is modeled using 2D surface conductivity (*J. Appl. Phys.*, 103 (2008), 064302) with a temperature of 300 K and a scattering rate of 0.001 eV.
Additionally, as the number of layers increases, the plasmon frequency also blue-shifts. For example, for an array with $D = 40$ nm and $P = 120$ nm, as the electrostatic doping increases from 0.2 to 0.7 eV, the plasmon of the monolayer shifts from $\sim 13900$ nm (THz) to $\sim 7300$ nm (mid-IR), respectively. For 6-layer graphene, the plasmon shifts from $\sim 6700$ nm (mid-IR) to $\sim 3090$ nm (close to NIR), respectively. By decreasing the diameter and periodicity, the plasmon frequency of these few-layer, anti-dot lattices can be blue-shifted into the NIR—opening new opportunities for graphene in tunable NIR plasmonics, beyond what has been achieved with dot arrays (ACS Nano, 7 (2013), 2388–2395).

Furthermore, we evaluate the plasmon frequency dependence on carrier concentration, fermi energy, and the dimensions of a graphene structure using the Drude model for metals and the scaling law for graphene dot structures (ACS Photonics, 1 (2014), 135–152).

With this work, we employ simulations to identify few-layer graphene nanomesh structures with broadly tunable optoelectronic responses from the THz to NIR, informing future experimental investigation of graphene as a NIR plasmonic material (Manuscript in preparation). Finally, we use the observed relations to provide design parameters for scaling the structure and propose schemes to further shift the plasmon response to shorter wavelengths.

**QN03.06.09**

**Elasto-Optic Properties of Co, Cu, Mo and Sn Intercalated α-MoO₃ as Measured by Brillouin Spectroscopy**

Daniel Williams, Bryan P. Moser, Nicholas Lundgren and Kristie Koski; University of California, Davis, Davis, California, United States.

Molybdenum trioxide ($\alpha$-MoO₃) is a 2D layered oxide that has shown suitability in electrochromic and photochromic devices owing to the tunability of its optical properties. Through reversible intercalation of zero-valent metals, the color of $\alpha$-MoO₃ can be altered from transparent white to dark blue. In this study we show how intercalation also changes the elasto-optic properties of $\alpha$-MoO₃ via intercalation of Sn, Cu, Mo, and Co. Brillouin spectroscopy is a non-invasive, non-contact, laser-based technique that can be used to measure the elastic properties of a material. We determine the full elastic stiffness tensor of $\alpha$-MoO₃ and show how intercalated metals alter the elastic properties.

**QN03.06.10**

**Chemically Tunable Acoustic Phonons in Intercalated Bi₂Se₃**

Nicholas Lundgren, Kristie Koski, Daniel Williams and Bryan P. Moser; Koski Group, University of California, Davis, Davis, California, United States.

Bismuth selenide is a 2D layered material with acoustic, optical, and electronic properties that can be chemically tuned through intercalation. Using Brillouin laser light scattering, we measure the acoustic phonons of metal-intercalated Bi₂Se₃. We show that the entire elastic stiffness tensor can be chemically tuned through intercalation of metals into this host. Acoustic attenuation, elasticities, and sound velocities are presented.

**QN03.06.11**

**Pressure-Dependent Raman of Mn-Intercalated 2D Layered Materials**

Virginia L. Johnson, Daniel Williams, Gabriella Lahti, Bryan P. Moser and Kristie Koski; University of California, Davis, Davis, California, United States.

Two-dimensional layered materials (2DLM), Bi₂Se₃, MoSe₂, Si₂Te₃, and GeSe were intercalated with atomic manganese and investigated to 7 GPa using a diamond anvil cell and Raman spectroscopy. There have only been a few studies of intercalation experiments at high pressure. Of those, most have focused on the effects of staging. The behavior of a specific intercalant in different hosts remains unexplored. These studies demonstrate that intercalation of manganese into 2DLMs can result in the appearance of new Raman peaks with pressure, and a change in the initial Raman frequency coincident with no change in the frequency shift with pressure.

**QN03.06.12**

**High-Pressure Study of Vibrational Structure in Phosphorene Samples**

Jacek B. Jasinski, Meysam Akhtar, Congyan Zhang, Manthilia Rajapakse, Rajib Musa, Ming Yu and Gaminu Samanasekera; University of Louisville, Louisville, Kentucky, United States.

In recent years, phosphorene, a two-dimensional (2D) form of elemental black phosphorus, has attracted a great deal of attention because of its unique properties and numerous potential applications. This material exhibits a highly tunable bandgap, high carrier mobility, and strong in-plane anisotropy. Its potential applications extend onto various fields, including electronic, optoelectronic and spintronic devices, sensors and actuators, as well as different energy conversion and storage technologies. Here, we report our recent study on the fabrication, characterization, and high-pressure properties of phosphorene samples. We used a diamond anvil cell and conducted a series of in-situ Raman spectroscopy measurements at pressures up to $\sim 10$ GPa. Simultaneous theoretical calculations, performed using the density functional theory (DFT) framework, as implemented in the Vienna Ab-initio Simulation Package (VASP), were also conducted. We used a short transport growth method for obtaining bulk black phosphorus, followed by the liquid mechanical exfoliation to produce flakes of phosphorene of different layer number thickness. These samples were thoroughly characterized using an array of structural and optical methods. For the in-situ high-pressure Raman experiments, two types of flakes, one with a few layers and the other with many layers, were selected. In both cases, systematic shifting of the primary Raman modes, i.e. $A_{1g}$, $E_{2g}$, and $A_{1g}$, with increasing pressure was observed. Such shifts were also found in our theoretical calculations. The detailed behavior and the magnitude of Raman shifts directly reflect the anisotropic nature of phosphorene, as well as the difference in the number of layers. Our study provides a better understanding of the relationship between the strain and the vibrational structure in phosphorene. Together with similar studies, it can enable rational strain engineering towards additional functionalities and device applications of phosphorene and other 2D materials.

**QN03.06.13**

**Magnetic Field Driven Metal Insulator Transition in Bi₂Te₃Se Topological Insulators**

Roshan Irfan; Physics, Aligarh Muslim University, Aligarh, India.

Topological insulators (TIs) are a new phase of matter with bulk insulating and conducting surface states. In three dimensional topological insulators such as Bi₂Se₃, large numbers of selenium vacancies push the Fermi level inside the conduction band; due to which the charge transport is generally dominated by the bulk current in this crystal and the as grown crystals of Bi₂Te₃ are p-type because of Te-Bi exchange defects. In order to extract the surface properties of topological insulators, it is necessary to have insulating bulk state in the TI material. Thus, among the known topological insulators, Bi₂Te₃Se with basic quintuple layer as Te-Bi-Se-Bi-Te, emerged as a promising material for studying the topological insulating properties. Bi₂Te₃Se is the hybrid material in which the selenium ion occupies the innermost layer in each quintuple. This will suppress both vacancy formation and Te-Bi exchange defects. In this report we study the surface properties of topological insulators Bi₂Te₃Se thin films grown by physical vapor deposition using Bi₂Te₃Se single crystals as a precursor. Pure phase of Bi₂Te₃Se are investigated using x-ray diffraction. Raman spectroscopy of Bi₂Te₃Se thin film showed strong intensity of $A_{1g}$, $E_{2g}$ and $A_{1g}$ modes in addition with $A_{1g}$ modes. The surface studies on these thin films were carried out using scanning electron microscopy and atomic force microscopy and the elemental analyses is done using x-ray photoelectron spectroscopy. The $R_{s}$ variation with temperature in the range 2 K to 350 K at different magnetic field shows a bump at high temperature and as we increase the magnetic field there is increase in resistance at high temperatures. The magneto-resistance measurements on Bi₂Te₃Se thin film shows a weak antilocalization effect that arises due to quantum interfering nature of topological insulators and the measured weak anti-localization effect is fitted using Hikami-Larkin-Nagaoka (HLN) model.

**QN03.06.14**

**Morphological Engineering and Site-Specific Positioning of MoS₂ Layered Structures—The Role of Au Seeding**

Xinqi Chen and Yuan Li; Northwestern University, Evanston, Illinois, United States.

Molybdenum disulfide (MoS₂), a semiconductor in the family of transition metal dichalcogenide (TMD) materials, has recently drawn great research interest in a wide range of applications such as electronic transistors, light sensing, batteries, and hydrogen production. However, the limited control over the geometry, location, yield, and size distribution of the products using current synthesis methods has severely limited their large-scale applicability. Herein, we identify the ability to use metal (e.g., Au) nanoparticles to seed the growth of MoS₂ layered structures (including lateral monolayer and vertical wings) and thereby provide a means to achieve programmable and controllable synthesis. In this study, pre-patterned Au seeds are used as heterogeneous nucleation sites to induce the formation of desired geometries of MoS₂ layers via chemical vapor deposition. Our experimental and theoretical results shed light on the growth mechanism driving the formation of MoS₂ monolayers at these sites, revealing that the “seeding effect” originates from the favorable formation energy of MoS₂ on the Au surface. A field-effect transistor with a pre-designed MoS₂ monolayer channel exhibits electronic performance that compares nicely with previously reported MoS₂ monolayer devices. The vertical wing-like MoS₂ layers, with an abundance of edge-terminated active sites, are found to exhibit dramatically
improved electrocatalytic activity for the hybrid evaporation reaction. We believe this study contributes fundamental insights into controlled synthesis of layered TMDs, making integration of these materials into emerging electronic and energy systems more attainable.

**QN03.06.15 Diversified Magnetoelectric Coupling in 2D Multiferroics** Qing Yang and Menghao Wu; Huazhong University of Science and Technology, Wuhan, China.

Multiferroic materials with coupled magnetism and ferroelectricity, even though scarcely exist in nature, are highly desirable for efficient “electric writing + magnetic reading”. Currently, the polarization and magnetization of traditional multiferroics with strong magnetoelectric coupling are all too weak for practical applications. Here we show first-principles evidences that strong magnetoelectricity can be realized in a series of 2D multiferroics: in some intercalated bilayer systems, their “mobile” magnetism can be controlled by ferroelectric switching upon external electric field, exhibiting either “on” state with spin-selective and highly p-doped channels, or “off” state insulating for both spin and electron transport, which renders efficient electrical writing and magnetic reading; vertical polarization can be maintained against depolarizing field, rendering high-density data storage possible; moreover, all those functions can be directly integrated into a 2D wafer, like n/p channels by doping in a silicon wafer. In some 2D systems, the magnetization can be switched by 90 or even 180 degree upon ferroelectric switching.


**QN03.06.16 Selective Growth of Bi$_2$Te$_3$/WS$_2$ Heterostructures with Emergent Properties** Ethan L. Kahn$^1$, Michael Lucking$^1$, Fu Zhang$^1$, Yu Lei$^2$, Kory Beach$^3$, Tomotaroh Granzier-Nakajima$^4$, Ana Laura Elias$^5$, Humberto Terrones$^1$; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2Physics, Rensselaer Polytechnic Institute, Troy, New York, United States.

To create complex, scalable device structures from 2D materials, it is necessary for patterned growth techniques to be developed. While several methods have been developed for the seeding or exclusion of 2D nucleation on conventional substrates (e.g. SiO$_2$ mica, sapphire), to date there have been few reports of patterned growth of one atomically thin material on top of another. Here, we demonstrate a low temperature (< 260 °C) and generalizable deposition technique for the selective-area growth of few-layer Bi$_2$Te$_3$ on chemical vapor deposition (CVD)-grown WS$_2$ single crystalline monolayers. These heterostructures are observed to grow with an epitaxial registry despite considerable lattice mismatch, and display both electronic and optical properties distinct from their constituent layers. These results are explained by Density Functional Theory calculations, which confirm that Bi$_2$Te$_3$/WS$_2$ possesses an electronic structure unique from the layers from which it is comprised. The nature of the interlayer electronic coupling in this novel system is explored further through computation of its band structure upon variation of both the interlayer distance and orientation.

**QN03.06.17 Increasing the Coverage of Functional Groups on Exfoliated Molybdenum Disulfide** Ellen X. Yan and Nathan S. Lewis; California Institute of Technology, Pasadena, California, United States.

Two-dimensional layered transition-metal dichalcogenides (TMDs) containing a Group V1 metal (MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$) have been explored recently for use in a variety of devices and applications, including transistors, ultra-thin flexible electronics, sensors, drug delivery, and bio-imaging. A variety of methods have been developed for covalent and non-covalent functionalization of the relatively inert basal plane of TMDs to improve their application-specific suitability. We are investigating the use of reductant-activated functionalization to increase the coverage of functional groups on covalently modified surfaces of 1T MoS$_2$ relative to existing methods, where one-electron reductants are used as sacrificial electron donors that can transfer negative charge to the MoS$_2$. The reduced MoS$_2$ can then react with electrophiles, similar to the transfer of negative charge from freshly intercalated and exfoliated MoS$_2$.

Our results for reductant-activated addition of methyl and propyl groups to 1T MoS$_2$ show that we are able to increase the coverage of these groups by 50-100% and facilitate functionalization with weak electrophiles using strong one-electron reductants. We also observe that the rate of reaction increases with increased reduction potential, resulting in higher coverages under the same conditions. Coverage of functional groups was quantified using XPS and TGA, and the covalent C-S bond and carbon species observed through FTIR and solid-state 13C-CPMAS NMR. By enabling greater coverage and facilitating reactions with weak electrophiles, reductant-activated functionalization is a promising method to broaden the set of obtainable functionalized TMD materials.

**QN03.06.18 Tuning the Opto Electronic Properties of Ultrasmooth Large Area rGO Films Grown via Pulsed Laser Deposition (PLD) Technique** Muhammed I. Manojittachali$^{1,2}$, M. S. Ramachandra Rao$^1$ and Venkatesan Thirumalai$^2$; 1Physics, IIT Madras, Chennai, India; 2NUSNRI, National University of Singapore, Singapore, Singapore.

We present the growth of large area ultrasmooth reduced graphene oxide (rGO) thin films on a four inch wafer via beam scanning mode of Pulsed laser deposition technique. With the versatility of the PLD technique, the easy tuning of optoelectronic properties is achieved on rGO thin films without employing any buffer layers. The conventional growth mechanism of rGO films involves hazardous chemicals, whereas this physical vapour deposition technique gives high quality rGO films with tunable optoelectronic properties. This wafer-scale growth mechanism of rGO films can potentially employ in various optoelectronic applications due to its high transparency and p-type conductivity. We illustrates the optoelectronic tunability of large area rGO films and its use through the evaluation of transparent conducting films, where our rGO films shows highest performance as compared to existing p-type transparent conducting films.

**QN03.06.19 Chemical Vapor Deposition of Bernal-Like Stacked Graphene with Built-in Vertical Electric Field** Minseek Yoo, Hyo Chan Lee and Kilwon Cho; Chemical Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

Multilayer graphene has been considered as a promising material for various optoelectronic devices because of its tunable electronic structure under an vertical electric field (E-field). Introduction of desired E-field inside the multilayer graphene is essential to fully exploit its intriguing electronic properties. However, applying desired E-field inside multilayer graphene has been remained challenge because external E-field is mostly screened by the outer graphene layer. Here, we report a one-step chemical vapor deposition for the synthesis of Bernal-like stacked graphene that S atoms are gradiently-doped in c-axis. The thickness and built-in E-field of synthesized graphene can be simultaneously controlled in wide range at the growth stage. We demonstrated tunability of electronic structure of synthesized graphene by dual-gate field-effect transistor and infrared absorption measurement. Taking advantage of built-in E-field, we fabricated barristor-type graphene photodetectors that has both high phororesponsivity and on/off current ratio.

**QN03.06.20 Quantum-Confined Stark Effect and Electric-Field Tuning of Excitons in 2D Ferroelectric α-InSe Layers** Jingqi Qiao$^1$ and Su Ying Quak$^{1,2}$; 1Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore, Singapore; 2Department of Physics, National University of Singapore, Singapore, Singapore.

The Stark effect in quantum-confined nanostructures can lead to electric field tuning of exciton energies and dissociation rates, and is important for applications in optoelectronic devices. Two-dimensional (2D) α-InSe has recently been demonstrated theoretically [1] and experimentally [2] to be a 2D ferroelectric material with out-of-plane polarization. However, the Stark effect in this ferroelectric material is largely unknown. Here, we perform first principles density functional theory and many electron perturbation theory GW-BSE (Bethe-Salpeter equation) calculations to investigate the effect of out-of-plane electric fields on the optical properties of 2D α-InSe. We find that the magnitude of the Stark shift depends sensitively on the direction of applied electric field, which results from the spontaneous polarization in the material. When the direction of the electric field is antiparallel to the intrinsic dipole moment, the exciton energies and band gaps decrease significantly even for the monolayer, at a rate that is comparable to that previously found
for interlayer excitons in 2D materials [3]. Our results will motivate experimental studies of the Stark effect in the 2D ferroelectric, α-InSe1.

QN03.06.21
2D Graphene Oxide Based Metal Hybrid Systems for Sensing and Catalysis Hadi Kelami and Mary Sajjini Devadas; Department of Chemistry, Towson University, Towson, Maryland, United States.

Graphene oxide (GO) serves as a precursor to various technologies, which include batteries, biosensors, solar cells, and supercapacitors. Metal hybrids of GOx enhance the sensitivity and electrical conductivity for sensing and catalytic applications. In this project we use silver and palladium nanoparticles independently to modify the surface of GOx. Silver nanoparticles exhibit optical properties that play a role in bacterial resistance, demonstrating its role in various biomedical sensors. Palladium nanoparticles are highly sensitive and functional in room temperature; making it an ideal metal for catalytic applications. Here we report the synthesis of functional graphene oxide from graphite flakes, followed by both successful carboxylation and reduction. In this experiment, carboxylation of GOx was followed by insertion of silver nanoparticles through an oleylamine ligand. Reduction of GOx resulted in a highly conductive, monolayer graphene quantum dot, which will be coated with palladium nanoparticles and utilized in catalytic applications, primarily Suzuki cross-coupling reactions. The Pd-GOx will serve as a cheaper and stable alternative as compared to traditional palladium-based catalysts used in these reactions. Initial results of our experiment will be presented.

We acknowledge funding from NSF MRI 1626326.

QN03.06.22
Ferrimagnetism of Ti-Adsorbed Graphene Zhenzhen Qin1 and Xu Zuo2; 1Zhengzhou University, Zhengzhou, China; 2Nankai University, Tianjin, China.

Using the first-principles calculations, we investigate the magnetism of isolated Ti-adsorbed graphene and the magnetic ground state of Ti adatoms at various concentrations. For isolated Ti adatom on graphene, we analyze the localization of magnetic impurity states and moment formation that can be understood in terms of hybridization between C-pz and Ti 4s-3d orbitals. To examine the magnetic ground state of Ti adatoms, we construct graphene cells with Ti adatom at various concentrations and set up the magnetic configuration for a triangle lattice. It is found that a ferrimagnetic (FI) phase is the most stable in a wide range of Ti concentration by comparing the total energies of different magnetic states. In addition, the exchange integrals between the nearest neighbor and next-nearest-neighbor Ti adatoms are calculated by applying a classical Heisenberg model. The prediction of a graphene-based FI metal monolayer will open the door to applications of spintronics, given that Ti obeys a 2-D growth mechanism on graphene.

QN03.06.23
Negative Poisson's Ratio in Two-Dimensional Honeycomb Structures Zhenzhen Qin1, Guangzhao Qin1 and Ming Hu1; RWTI Aachen University, Aachen, Germany; 2Zhengzhou University, Zhengzhou, China; 3University of South Carolina, South Carolina, South Carolina, United States.

Negative Poisson's ratio (NPR) in auxetic materials is of great interest due to the typically enhanced mechanical properties, which enables plenty of novel applications. In this paper, by employing first-principles calculations, we report intrinsic NPR in a class of two-dimensional honeycomb structures (graphene, silicene, h-BN, and h-GaN), which are distinct from all other known auxetic materials. They share the same mechanism for the emerged NPR despite the different chemical composition, which lies in the increased bond angle θ. However, the increase of bond angle θ is quite intricate and anomalous, which cannot be explained only in the point of view of the geometry structure and mechanical response, such as in the framework of classical molecular dynamics (MD) simulations based on empirical potential. We attribute the counter-intuitive increase of θ and the emerged NPR fundamentally to the strain modulated electronic orbital coupling and hybridization. Furthermore, we propose that the NPR phenomenon can also emerge in other nanomaterials or nanostructures with similar honeycomb structure. The physical origin as revealed in our study deepens the understanding on the NPR and would shed light on future design of modern nanoscale electromechanical devices with special functions based on auxetic nanomaterials and nanostructures.

QN03.06.24
Graphene-MoS2 Heterostructures for Infrared Photodetection Audrey Rose M. Gutierrez, Dehui Zhang, Zhe Liu and Zhaozhong Zhong; University of Michigan, Ann Arbor, Michigan, United States.

Infrared imaging has applications in multiple fields, including point-of-care diagnostics in medical care and gas sensing in air quality monitoring. While solutions for these applications exist, commercially available technologies are expensive due to reliance on costly materials. Here we report an inexpensive and scalable device for infrared sensing, implemented using chemical vapor deposition (CVD) grown two-dimensional materials. A MoS2 field-effect transistor (FET) is combined with a graphene photoactive layer, allowing transport of charges through a tunable Schottky barrier. The MoS2 FET has a lower dark current and higher on-off current ratio than graphene alone, while the graphene component permits detection of light beyond the natural absorption spectra of MoS2. The resulting heterostructure device is capable of broadband detection. Detailed mechanism, device sensitivity, and viability for photodetector array applications will be discussed in the presentation.

QN03.06.25
Synthesis, Structure and Stability of Siloxetine Nanosheets Tuahit Shah1, Karalee Jarvis1, Pengyi Tang2, Eric Prestat1, Jordi Arbiol1, Quentin Ramasse1 and Brian A. Korgel1; 1McKetta Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, Texas, United States; 2Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, Spain; 3SuperSTEM Laboratory, Daresbury, United Kingdom; 4Texas Materials Institute, The University of Texas at Austin, Austin, Texas, United States.

Silicene, a buckled honeycomb structure of Si atoms, has received increased interest in recent years because of its exotic properties and compatibility with existing semiconductor technology. Theoretical studies have predicted silicene to be thermodynamically stable, but its synthesis remains a challenge due to the high reactivity of sp2 hybridized Si structures. So far, silicene has been synthesized on a metal substrate under ultra-high vacuum. The major drawback of this method is the high reactivity of silicene surface and its strong coupling with the metal substrate. A promising alternative is the synthesis of functionalized silicene that can preserve the honeycomb structure of silicene and reduce its surface reactivity. Functionalized silicene can be synthesized using a top-down method starting with siloxene. Siloxene is a layered, honeycomb silicon structure with hydride and hydroxide functionalization. Previous research has focused on the hydrosilylation reaction of siloxene as an exfoliation method. In our work, we show that stable dispersions of siloxene nanosheets can be synthesized via liquid-assisted exfoliation without hydrosilylation and conduct a detailed study of their structure and stability.

Electronic Energy Loss Spectroscopy (EELS) and Electron Diffraction show that the structure of siloxene nanosheets is sensitive to air exposure. The nanosheets synthesized in ambient environment show amorphous silica-like characteristic while in the inert synthesis they retain the hexagonal crystalline structure. Our in-depth EELS study shows that crystalline nanosheets have a signature distinct from pure Si and SiO2. We have also identified a method for the large-scale synthesis of these nanosheets which enables size-selection. This study, conducted in ambient environment, shows a blue shift in the band-gap and luminescence decrease in size of the nanosheets likely due to a combined effect of oxidation and size. This method can be potentially extended to the synthesis in inert environment to yield size-selected dispersions of crystalline siloxene nanosheets. In this work, we provide the first EELS study of siloxene nanosheets to understand its structure and stability in different environments. We have also identified a unique solution-based synthesis method and the conditions under which crystalline siloxene nanosheets can be obtained. This provides a feasible synthesis for silicon-based nanosheets and opens up the possibility of integrating them with the existing silicon technology.

QN03.06.26
Anomalously Temperature-Dependent Thermal Conductivity of Monolayer GaN with Large Deviations from the Traditional 1/T Law Guangzhao Qin and Ming Hu; University of South Carolina, Columbia, South Carolina, United States.

Efficient heat dissipation, which is featured by high thermal conductivity, is one of the crucial issues for the reliability and stability of nanodevices. However, due to the generally fast 1/T decrease of thermal conductivity with temperature increase, the efficiency of heat dissipation quickly drops down at an elevated temperature caused by the increase of work load in electronic devices. To this end, pursuing semiconductor materials that possess large thermal conductivity at high temperature, i.e., slower decrease of thermal conductivity with temperature increase than the traditional α ∼ 1/T relation, is extremely important to the development of disruptive nanoelectronics. Recently, monolayer gallium

QN03.06.27
Negative Poisson's Ratio in Two-Dimensional Honeycomb Structures Zhenzhen Qin1, Guangzhao Qin1 and Ming Hu1; RWTI Aachen University, Aachen, Germany; 2Zhengzhou University, Zhengzhou, China; 3University of South Carolina, South Carolina, South Carolina, United States.

Negative Poisson's ratio (NPR) in auxetic materials is of great interest due to the typically enhanced mechanical properties, which enables plenty of novel applications. In this paper, by employing first-principles calculations, we report intrinsic NPR in a class of two-dimensional honeycomb structures (graphene, silicene, h-BN, and h-GaN), which are distinct from all other known auxetic materials. They share the same mechanism for the emerged NPR despite the different chemical composition, which lies in the increased bond angle θ. However, the increase of bond angle θ is quite intricate and anomalous, which cannot be explained only in the point of view of the geometry structure and mechanical response, such as in the framework of classical molecular dynamics (MD) simulations based on empirical potential. We attribute the counter-intuitive increase of θ and the emerged NPR fundamentally to the strain modulated electronic orbital coupling and hybridization. Furthermore, we propose that the NPR phenomenon can also emerge in other nanomaterials or nanostructures with similar honeycomb structure. The physical origin as revealed in our study deepens the understanding on the NPR and would shed light on future design of modern nanoscale electromechanical devices with special functions based on auxetic nanomaterials and nanostructures.
nitride (GaN) with a planar hexoncomb structure emerges as a promising new two-dimensional material with great potential for applications in nano- and optoelectronics. Here, we report that, despite the commonly established 1/7 relation of thermal conductivity in plenty of materials, monolayer GaN exhibits anomalous behavior that the thermal conductivity almost decreases linearly over a wide temperature range above 300 K, deviating largely from the traditional $\kappa \sim 1/T$ law. The thermal conductivity at high temperature is much larger than the expected thermal conductivity that follows the general $\kappa \sim 1/T$ trend, which would be beneficial for applications of monolayer GaN in nano- and optoelectronics in terms of efficient heat dissipation. We perform detailed analysis on the mechanisms underlying the anomalously temperature-dependent thermal conductivity of monolayer GaN in the framework of Boltzmann transport theory and further get insight from the view of electronic structure. Beyond that, we also propose two required conditions for materials that would exhibit similar anomalous temperature dependence of thermal conductivity: large difference in atom mass (huge phonon band gap) and electronegativity (LO-T0 splitting due to strong polarization of bond). Our study offers fundamental understanding of phonon transport in monolayer GaN, and the insight gained from this study is of great significance for the design and search of materials superior for applications in nano- and optoelectronics in terms of high-performance thermal management.

QN03.06.27

Synthesis and Optoelectronic Applications of Heterostructures Based on Carbon Nanomaterials and MoS$_2$

Van Tu Nguyen and Ji-Yong Park; Ajou University, Suwon, Korea (the Republic of)

By employing 2-step chemical vapor deposition (CVD) method, we realize heterostructures of molybdenum disulfide (MoS$_2$) with carbon nanomaterials such as graphene and carbon nanotubes (CNTs). On the first CVD step, either highly aligned CNTs (HA-CNTs) or graphene is first synthesized. On the second CVD step, mono to few-layer MoS$_2$ is directly grown on previously grown carbon nanomaterials forming heterostructures. In the case of HA-CNTs, MoS$_2$ grows preferentially along CNTs, forming mixed-dimensional heterostructures, which become visible as line-like features under an optical microscope. Post-growth characterizations such as atomic force microscopy, Raman and PL measurements confirm the formation of heterostructures with mostly few-layer crystalline MoS$_2$ flakes along HA-CNTs with low defect densities. On the other hand, vertical heterostructures of graphene/MoS$_2$ are prepared by the CVD deposition of triangular MoS$_2$ flakes on the graphene surface. Efficient charge transfer from MoS$_2$ to carbon nanomaterials are found on both types of heterostructures. By utilizing efficient light absorption and charge transfer in MoS$_2$, with high mobility channels (CNT or graphene), we demonstrate photodetectors with high responsivities using both types of heterostructures. Strategies to improve the temporal responses of photodetectors will also be discussed.

QN03.06.28

Role of CVD-Graphene Layer Between Current Collector and Active Electrode Material Towards Equivalent Series Resistance in Supercapacitors

Sunil Kumar$^1$ and Yongho Seo$^2$

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Graphene has been used in supercapacitors as an electrode material in recent times due to its high surface area. The reduced graphene oxide (rGO) has a high surface area, which is a key parameter for high capacitance. In addition, there is another parameter i.e. equivalent series resistance (ESR), which influences the performance of supercapacitors. ESR should be controlled, particularly at high scan rates, for the high capacitance of the electrical double layer capacitors (EDLC). The resistance at the interface between the current collector and the active electrode material is the major component of ESR. In this report, chemical vapor deposition (CVD) method grown graphene has been introduced between the rGO and Ni-foil to minimize this resistance. The GGO having the surface area, ~367 m$^2$/g, has been used as an active electrode material and Ni-foil as the current collector. The CVD-graphene, grown directly on Ni-foil at various cooling rates i.e. 20, 40 and 100 $^0$C/min. during the growth process, has been used between rGO and Ni-foil to fabricate electrodes for optimizing the supercapacitor properties. The electrodes with CVD-graphene grown at faster cooling rates exhibited better electrochemical characteristics even at high scan rates. The specific areal capacitance of electrodes with CVD-graphene grown at 40 $^0$C/min. cooling rate is 58.3 F/cm$^2$ (213.8 $F$/$g$) and 39.1 F/cm$^2$ (143.3 $F$/$g$) at scan rates 0.05 and 10 $V$/$s$, respectively. The electrodes with CVD-graphene grown at 100 $^0$C/min. exhibit better stability, and low voltage drops at various current densities while maintaining quasi-rectangular shapes in C-V characteristics. The introduction of CVD-graphene between the rGO and Ni-foil reduced the ESR significantly from 0.8 $\Omega$ to ~0.38 $\Omega$ at high frequencies.

QN03.06.29

Integration of Partially Suspended Monolayer Graphene into a Strain-Based Polymer Chemiresistor

Annelise C. Thompson, Kyra Lee and Nathan S. Lewis; California Institute of Technology, Pasadena, California, United States.

Graphene has been used in supercapacitors as an electrode material in recent times due to its high surface area. The reduced graphene oxide (rGO) has a high surface area, which is a key parameter for high capacitance. In addition, there is another parameter i.e. equivalent series resistance (ESR), which influences the performance of supercapacitors. ESR should be controlled, particularly at high scan rates, for the high capacitance of the electrical double layer capacitors (EDLC). The resistance at the interface between the current collector and the active electrode material is the major component of ESR. In this report, chemical vapor deposition (CVD) method grown graphene has been introduced between the rGO and Ni-foil to minimize this resistance. The GGO having the surface area, ~367 m$^2$/g, has been used as an active electrode material and Ni-foil as the current collector. The CVD-graphene, grown directly on Ni-foil at various cooling rates i.e. 20, 40 and 100 $^0$C/min. during the growth process, has been used between rGO and Ni-foil to fabricate electrodes for optimizing the supercapacitor properties. The electrodes with CVD-graphene grown at faster cooling rates exhibited better electrochemical characteristics even at high scan rates. The specific areal capacitance of electrodes with CVD-graphene grown at 40 $^0$C/min. cooling rate is 58.3 F/cm$^2$ (213.8 $F$/$g$) and 39.1 F/cm$^2$ (143.3 $F$/$g$) at scan rates 0.05 and 10 $V$/$s$, respectively. The electrodes with CVD-graphene grown at 100 $^0$C/min. exhibit better stability, and low voltage drops at various current densities while maintaining quasi-rectangular shapes in C-V characteristics. The introduction of CVD-graphene between the rGO and Ni-foil reduced the ESR significantly from 0.8 $\Omega$ to ~0.38 $\Omega$ at high frequencies.

QN03.06.30

Annealing Effects on Direct Bandgap Emission from Atomically Thin MoS2 via NB Ion Implantation

Gourav Bhuyan$^1$ and Mengbing Huang$^1$; $^1$Colleges of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York, United States; $^2$University at Albany, State University of New York, Albany, New York, United States.

The emergence of 2D materials has led to increased attention on correlating the structural, optical, and optoelectronic properties of atomically thin transition metal chalcogenides like MoS$_2$. We demonstrate the tunability of the photoluminescence (PL) properties of bulk MoS$_2$ via implantation of Nb ions. Raman spectroscopy is used to confirm the p-type doping. The PL intensity of MoS$_2$ is drastically enhanced by the adsorption of p-type dopants. X-ray photoelectron spectroscopy (XPS) is used to study the change of MoS$_2$ structure after annealing in oxygen. We also demonstrate a stronger PL enhancement through defect engineering and oxygen bonding realized by oxygen anneal. Our results provide a new route for modulating the optical properties of two-dimensional semiconductors. The strong and stable PL from defects sites of MoS$_2$ may have promising applications in optoelectronic devices.

QN03.06.31

Novel Graphene Functionalization Approach Leading to Ultrasensitive, Robust and Fast Sulfur Contaminants Detection in Aviation Fuels

Evelynia Lock$^1$, Keith Perkins$^1$, Joseph Prestigiacomo$^1$, Anthony Boyd$^1$, Anindya Nath$^1$, Mike Ososky$^1$, Rachael L. Myers-Ward$^1$, Pratibha Deb$^1$, Thomas Reinecke$^1$ and D. K. Gaskill$^1$; Naval Research Laboratory, Washington, District of Columbia, United States; $^2$George Mason University, Washington, District of Columbia, United States; $^3$Howard University, Washington, District of Columbia, United States.

In this work we demonstrate novel functionalization approach allowing for increased reactivity of epitaxial graphene with no deterioration of electrical properties. In particular, we show that these functionalized samples exhibit the Quantum Hall Effect and possess Shubnikov-de
Haas oscillations, which are typical for high quality exfoliated graphene flakes. We did not observe these phenomena on the initial pristine epitaxial graphene films. From first principle calculations, these results are likely due to reduced sheet charge density after functionalization, derived from charge transfer from the chemical molecules to the epitaxial graphene. For practical application, this means that graphene is amenable to attachment of other moieties (molecules, biomolecules, quantum dots, etc.). In this work, we show graphene films and sensors functionalization with ITO, ZnO, CuO, and Fe3O4 nanoparticles. We use these sensors for detection of sulfur contaminants in aviation fuel to prevent catalyst poison that rapidly degrades fuel cell performance. We demonstrate fast (≤ 30 seconds) response, with ppb levels of sensitivity and selectivity towards various sulfur compounds in synthetic S8 fuel mixtures (Figure 1). Furthermore, we show a path towards development of sensor arrays allowing chemical fingerprinting of complex mixtures. In addition, we perform principle component analysis allowing identification of unknown sulfur compounds based on developed library of responses. This work is partially supported by the Office of Naval Research through Naval Research Laboratory Base Program.

QN03.06.32
Double Gate Single Layer MoS2 FETs for Low Noise Frequency Modulation
Michael A. Rodder and Ananth Dodabalapur; University of Texas at Austin, Austin, Texas, United States.

Before the discovery and creation of molecularly thin, stable, semiconducting transition metal dichalcogenide (TMD) sheets, FETs with multiple independent gates were realized mostly by use of ultra-thin SOI channels. Due to the van der Waals attraction between a single layer sheet of TMDs (e.g. MoS2) and atomically smooth, defect free, insulating hexagonal boron nitride (h-BN), single layer MoS2 FETs with two gates (above and below the channel), to independently control the charge concentration in the channel, can be fabricated using standard dry transfer techniques developed for the construction of van der Waals bonded FETs made from TMDs and h-BN [1-2]. The functionality of these devices as circuit elements is of great interest.

In this work, we focus on fabricating single layer MoS2 FETs with two independent gates for use as front-end single transistor mixers to up-convert weak, low frequency input signals to a higher frequency of around 5 kHz. Chopper stabilization is a circuit technique that uses frequency modulation to up-convert a low frequency input signal, such as a brainwave, to a higher frequency (> 5kHz) where there is a reduction in 1/f noise before further amplification (i.e. using an op-amp). We show that a single layer, double gate MoS2 FET can be used as a chopper amplifier. The input signal of around 100Hz is applied to one of the two gates of the MoS2 FET. A modulation frequency of a few kHz is applied to the second gate. Heterodyning is observed albeit with a low conversion gain due to linearity created by large contact resistance. We improve the non-linearity ($I \sim V^2$ saturation characteristics) by increasing the channel length of our FETs so that the contact resistance does not dominate the total resistance. We note that a differential pair of double gate MoS2 FETs requires less overall FETs (two) as compared to the traditional chopper consisting of four silicon FETs. The pristine interfaces between MoS2 and h-BN could result in less noise caused by interface states as compared to traditional semiconductors. We also note that due to the van der Waals bonding of MoS2 and h-BN, these two-dimensional materials can be fabricated on a variety of substrates, making them of interest for front-end input signal frequency modulation. A biomedical signal may be acquired by use of an electrode gel sticking to a part of the body. Along with using two traditional metal gates to modulate the charge of the MoS2 channel, we will show results of an single transistor MoS2 chopper amplifier in which one of the gates is a traditional metal gate while the other is replaced with an ion-gel for charge modulation via ion-gating. By applying a low frequency input signal to the ion-gel gate while applying a few kHz signal to the traditional metal gate to show up-conversion of the input signal, we demonstrate the double gate MoS2 FET’s broader applications as a chopper amplifier to up-convert biomedical signals. Additionally, we present a new double gate MoS2 FET device structure for reducing contact resistance. From the necessity for electrostatic gating to reduce source/drain contact resistance in intrinsically low doped TMD FETs, we fabricate a double gated FET in which MoS2 is both on top and bottom of the source and drain metal, thereby resulting in electrostatic doping of the contact regions from both the top and bottom gate rather than only one gate as in the traditional double gate MoS2 FET structure. This new structure is made possible due to the van der Waals attraction between TMD and h-BN layers; such a structure could not be fabricated easily using conventional semiconductor materials.


QN03.06.33
High-Throughput Identification of Efficient Crystalline Solar-Cell Materials—Example of Screening 2D-Bulk Materials
Komal Choudhary; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

We present the results of a density functional theory high-throughput screening approach for identifying potential solar cell materials. In order to evaluate a materials efficiency, we calculate spectroscopy limited maximum efficiency (SLME) using frequency dependent dielectric function data obtained using meta-GGA TBmBJ formalism. Additionally, we use effective carrier mass information to further screen candidate materials. Finally, we present the results of a specific example screening case for finding potential 2D-bulk solar materials with high-SLME. Out of 30000 materials in the JARVIS-DFT database, we have 15000 TBmBJ frequency dependent dielectric function data. The dielectric functions were used to calculate SLME. We further investigate the elements that contribute towards high efficiency solar cell materials. We find elements such as Pd, Cu, In, Se, S are some of them. Furthermore, we screened 58 2D-bulk materials with high-SLME, low effective mass, and energy above convex hull ~0.1 eV/atom.

QN03.06.34
Interfacial Charge Behavior Modulation in Perovskite Quantum Dot-Monolayer MoS2 0D-2D Mixed-Dimensional van der Waals Heterostructure for Ultrason-sensitive Photodetector
Hualin Wu1, Zhuo Kang1 and Yue Zhang2; 1 School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China; 2 Beijing Municipal Key Laboratory of New Energy Materials and Technologies, University of Science and Technology Beijing, Beijing, China.

Fundamental understanding of charge behavior inside heterostructures is of vital importance for advancing high-performance optoelectronic applications. However, photoexcited state charge behavior at 0D-2D mixed-dimensional van der Waals heterostructures (MvdWHs) remains elusive. In this work, energy band alignment protocol was adopted to realize effective energy band structure engineering inside 0D-2D MvdWHs of perovskite quantum dots (QDs) and MoS2 monolayer with precisely designed typical type I and II heterostructures. The interfacial photoinduced charge behavior was probed and in-depth understood based on such MvdWHs from two opposite perspectives. Sufficient comparison of a series of optical characteristics results, including Raman shift, quenched photoluminescence, visualized suppressed fluorescence intensity, and imaged shortened fluorescence lifetime, clearly verified that the interfacial charge behavior can be tailored by varied band alignment in 0D-2D MvdWHs. Furthermore, the photoreponse performance and the relatively stronger and weaker photogating effects of such MvdWHs based phototransistors also demonstrated the modulation of interfacial charge behavior in 0D-2D MvdWHs via energy band structure engineering is still practicable for optoelectronic performance optimization. These results are expected to shed light on designing novel functional devices and advancing the development of 0D-2D MvdWHs in the foreseeable future.

QN03.06.35
Electronic, Topological and Phonon Dispersion Behaviour in vdW Layered Two-Dimensional Heterostructures
Sushant K. Behera and Pritam Deb; Tezpur University, Tezpur, India.

Two-dimensional (2D) materials offer a platform that allows creation of heterostructures with a variety of properties [K. S. Novoselov et al. *Science*, 353 (2016) 461]. Modelled van der Waals (vdW) heterostructures constitute an emerging field promising to design systems with properties on demand. Besides, specific electronic, topological, phononic and optical properties are convenient for controlling the generation, transportation and recombination of charge carriers, excitons, photons which are beneficial for the design of unique electronic devices and catalysts [A. K. Geim et al. *Nature*, 499 (2013) 419]. To assemble the vdW heterostructures, which consist of atomically sharp interfaces and atomic layered structures, provides the chance for engineering a new device at quantum length scale, so as to invent the ultarhin, low-power and flexible device. Despite the relatively weak vdW interaction, which does not affect the electronic properties around the Fermi level, the first principle calculations show significant changes in electron-phonon interaction trends in...

Acknowledgement
Department of Science and Technology, Govt. of India for DST-INSPIRE SRF Fellowship (IF150325). Tezpur University for providing HPCC Facility to perform simulation.

QN03.06.36
**Aligned Growth of Millimeter-Size Hexagonal Boron Nitride Single-Crystal Domains and Its Application for Deep Ultraviolet Photodetectors**
Jinhua Meng, Xing Wang Zhang, Heng Liu and Menglei Gao; Key Lab of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China.

Atomically thin hexagonal boron nitride (h-BN), a structural analogue of graphene, has received considerable special attention in recent years. As the unique insulator in the 2D family, h-BN has large optical band gap (5.97 eV), self-terminating surface, low dielectric constant, high thermal conductivity, superb mechanical strength and excellent chemical inertness, thus giving rise to a variety of applications, such as deep ultraviolet optoelectronic devices, dielectric substrates, or protective coatings. For both device applications and fundamental studies, high quality and large-area h-BN layers are certainly desirable. Although, numerous efforts have been devoted to synthesize h-BN domains, the lateral dimensions of single-crystal h-BN domains is still very small, only about one hundred micrometers. In this work, we demonstrated the aligned growth of millimeter-size single-crystal h-BN domains on the epitaxial Ni (111)/sapphire substrates by ion beam sputtering deposition. Under the optimized growth conditions, the single-crystal h-BN domains up to 0.6 mm in edge length were obtained. The formation of large-size h-BN domains results mainly from the reduced Ni-grain boundaries and the improved crystallinity of the Ni film. Furthermore, due to the close lattice match between h-BN and Ni (111), these h-BN domains exhibit well-aligned orientation. The merged h-BN layer exhibits quite uniform and excellent dielectric behavior. In addition, a high-performance deep ultraviolet (DUV) photodetector were fabricated based on the transferring h-BN layers on SiO$_2$/Si substrates, and the corresponding photodetectors exhibited high performance with an on/off ratio of $>10^4$ under DUV light illumination at 212 nm and a cutoff wavelength around 225 nm. This work provides an effective approach for synthesizing large-scale high-quality h-BN layers for electronic applications, especially for the construction of high-performance solar-blind photodetectors.

QN03.06.37
**ZnO/rGO Heterostructures as Potential Photomemristor**
Surinder P. Singh and Manjit Singh; CSIR-National Physical Laboratory, New Delhi, India.

The quest towards miniaturization and smart futuristic technologies in electronic, optoelectronic, healthcare and environmental technologies has fuelled research in material science and engineering. The memristive/ resistive switching devices are a promising candidate for upcoming innovations in electronics with high packing density. Recently, it is being envisioned that an optical control over memristors may open new paradigms in optoelectronic devices for photonic integrated circuits, optical fibre telecommunications, neuromorphic computing and artificial intelligence. Graphene and ZnO nanostructures as optically active semiconductors have already been studied in designing memristor/ resistive switches as well as photodetectors, individually. This encouraged us to further design a photomemristor using the two. We have prepared ZnO/rGO heterostructure using wet chemistry and spin coating the materials on ITO coated glass substrate. In heterostructure device, ZnO acts as a photoconducting layer, whereas, rGO film serves as a light absorbing material and an efficient (top) transport layer that facilitates the movement of charge carriers across the interface. The device showed a resistive switching behaviour with $I_{ON}/I_{OFF}$ ratio of $\sim 10^4$ and photoswitching with $I_{ON}/I_{OFF}$ ratio of $\sim 10^4$ under 370 nm illumination. The results indicate that ZnO/rGO heterostructures may form promising photomemristors.

8:00 AM QN03.07.01
**Quantum Calligraphy—Writing Single Photon Emitters in a Two-Dimensional Materials Platform**
Matthew R. Rosenberger$^2$, Chandrikier K. Dass$^2$, Hsun-Jen Chuang$^1$, Saujan Sivaram$^1$, Kathleen M. McCready$^1$, Joshua Hendrickson$^1$ and Berend Jonker$^1$; U.S. Naval Research Laboratory, Washington, District of Columbia, United States; $^1$Air Force Research Laboratory, Wright-Patterson AFB, Ohio, United States; $^2$KBRWyle, Beavercreek, Ohio, United States.

We present a paradigm for encoding strain into two dimensional materials (2DM) to create and deterministically place single photon emitters (SPEs) in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope (AFM) tip, the polymer layer plastically deforms. While the AFM tip is in contact with the sample, the AFM tip forces the 2DM to deform with the polymer layer, resulting in tensile strain build-up in the 2DM. When the AFM tip is removed, the adhesive interaction between the polymer and the 2DM prevents the 2DM from relaxing back to its original, strain-free geometry, resulting in a permanent and highly localized strain field in the 2DM. We demonstrate control of indent size by modifying the applied load. Also, we show excellent repeatability of both indent shape and size. We show that SPEs are created and localized at nanodots in a WSe$_2$/PMMA structure, as confirmed by antibunching measurements. The SPEs exhibit single photon emission up to 60 K, which is the highest temperature reported for SPEs in WSe$_2$. This *quantum calligraphy* allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities, and plasmonic structures. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

Reference:

8:15 AM QN03.07.02
**Tuning Thermal Transport in Two-Dimensional Ferromagnetic CrI$_3$ by Spin-Lattice Coupling**
Guangzhao Qin and Ming Hu; University of South Carolina, Columbia, South Carolina, United States.

Recently, two-dimensional monolayer chromium triiodide (CrI$_3$) with intrinsic magnetism was experimentally discovered, which shows promising applications in many technologies ranging from sensing to data storage where thermal transport plays a critical role. However, so far, the effect of spin-lattice coupling on the thermal transport properties has not been explored yet. In this talk, I will present the giant effect of spin-lattice coupling on the lattice thermal conductivity ($\kappa_l$) of monolayer CrI$_3$. The lattice thermal conductivity is more than two orders of magnitude enhanced by considering the spin-lattice coupling. The effect is found to be especially stronger for the acoustic phonon modes, which dominates thermal transport with spin-lattice coupling. The mechanism lies in the weakened phonon anharmonicity by spin-lattice coupling. The bond angle and atomic position are changed due to the spin-lattice coupling, making the structure much stiffer and more symmetric, which lead to the weaker phonon anharmonicity, and thus the enhanced thermal conductivity. This study uncovers the effect of spin-lattice coupling on the thermal transport, which would deepen our understanding on thermal transport and shed light on future research of thermal transport in magnetic materials.

8:30 AM QN03.07.03
**The Effect of Layer-Coupled States on Charge Transfer in van der Waals Heterostructures**
Peyman Zarehski$^1$, Yaqing Wei$^2$, Run Long$^3$ and Hui Zhao$^1$; Department of
Using semiconductor van der Waals materials in the ultrathin limit as a foundation for engineering new function in electronic materials, we demonstrate the tunable properties provided by direct growth and/or assembly of 0-D materials (quantum dots and organic molecules) on 2D materials (transition metal dichalcogenides and metal monochalcogenides). We address the challenge of controlling nucleation and growth on a non-reactive (vdW) substrate by developing a range of substrate pre-treatments prior to initiating van der Waals epitaxy via metal organic vapor phase deposition. Furthermore, the alternate pulsing of precursors enables the realization of self-limited growth using physisorbed species. We use this approach to grow p-type SnS on n-type MoS2 in both 2-D/2-D and 0-D/2-D heterojunctions. To understand the role of shape, size, structure, and composition on the physical behaviors and device characteristics of mixed-dimensional heterojunctions, we employ Kelvin probe force microscopy, conductive atomic force microscopy, and scanning photocurrent microscopy to analyze the induced photovoltage and photocurrent generated by these mixed-dimensional van der Waals heterojunctions. Further chemical tunability of the photoresponse is enabled by the direct deposition and assembly of organic donor or acceptor molecules on 2-D n-type or p-type materials, respectively, with subsequent characterization by scanning probes. While the energies of molecular orbitals and band edges can in general be used to predict the response, we find that local electrostatic effects at these unusual interfaces also play a role. Finally, in operando studies of the effects of adsorbing dopant molecules and metal oxide precursors will be described to provide new insights into mechanisms that enable tunable doping.

References:
sulfur vacancies, which is evident of the existence of local magnetic states. In a device environment, interacting strongly with the local magnetic defects through the Kondo effect, most of the electrons anomalously scattered back to the hot side, leading to a large anomalous positive Seebeck coefficient in highly conducting n-type MoS₂. Furthermore, modulated by an external electric field, a record power factor of 50 mW/mK² was achieved. Our device is planar and compact and could become a viable option for high-performance thermoelectric devices.

10:00 AM BREAK

10:30 AM *QN03.07.08 Tunable Symmetries and Berry’s Phase in Few Layer Graphene Mandar Deshmukh; TIFR, Mumbai, India.

There have been extensive studies on monolayer graphene where unique properties result from the symmetry of the honeycomb lattice. Few layer graphene systems are of interest as they offer interesting opportunities to study effect of electronic interactions [1] due to flatter bands while monolayer graphene was largely understood in terms of independent electron picture. In addition, few layer graphene offer an opportunity to break simple symmetries and study their consequence [2].

Berry’s phase can be probed using magneto-transport measurements. These measurements can throw up interesting questions in multiband system of few layer graphene. I will briefly discuss our efforts to measure and understand Berry’s phase in a complex multiband system.


11:00 AM *QN03.07.09 Optically Addressable Spin Defects in Hexagonal Boron Nitride Lee C. Bassett; Quantum Engineering Laboratory, Department of Electrical & Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Two-dimensional materials hosting optically addressable electronic states offer a unique platform for quantum engineering due to intrinsic spatial confinement and the ability to create multifunctional layered materials. Defect-related quantum emitters exhibiting room-temperature photoluminescence (PL) have been identified in the wide-bandgap van der Waals material hexagonal boron nitride (h-BN), although many questions remain regarding the defects’ chemical and electronic structure [1], and evidence for spin-related effects has so far been elusive. In this talk I will present new measurements of room-temperature, spin-dependent quantum emission in h-BN [2]. Select defects exhibit striking, anisotropic PL modulations in response to an applied magnetic field, with corresponding changes in the photon emission statistics consistent with an electronic model featuring a spin-dependent inter-system crossing between triplet and singlet states. The discovery of optically addressable spins in h-BN ushers in a new platform for spin-based quantum technologies with the potential for atom-scale engineering and versatile functionality.


This work was supported by the Army Research Office (W911NF-15-1-0589).

SESSION QN03.08/QN01.06/QN02.05: Keynote: Joint Session: 2D Magnets and Heterostructures
Session Chair: Srinivas Rao Singamaneni
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 129 A

11:30 AM *QN03.08.01/QN01.06.01/QN02.05.01 2D Magnets and Heterostructures Xiaodong Xu; University of Washington, Seattle, Washington, United States.

The recent discovery of 2D magnets provides new ways to study 2D magnetism by harnessing the unique features of atomically-thin materials, such as electrical control for magnetoelectronics and van der Waals (vdW) engineering for novel interface phenomena. In this talk, I will describe our recent magneto-optical spectroscopy experiments on vdW magnets. I will discuss the layered antiferromagnetic properties of CrI₃ with electrical control, giant tunneling magnetoresistance through spin filtering effect in vdW magnetic tunnel junctions, magnetic dynamics in zigzag antiferromagnets, and progress on exfoliable 2D magnets with stable magnetic order near room temperature.

SESSION QN03.09: Strain Effects and Opto-Electro-Mechanical Devices
Session Chairs: SungWoo Nam and Ursula Wurstbauer
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 129 A

1:30 PM QN03.09.01 Highly Mechanosensitive Ion Channels in 2D Membranes Alex Smolyanitsky and Alta Fang; National Institute of Standards and Technology, Boulder, Colorado, United States.

The ability to tune aqueous ion conduction across nanoporous membranes is a key ingredient in a wide variety of applications in nanofluidics and is a critical function of protein ion channels, which control salinity in living cells for a myriad of biological processes. Unsurprisingly, the inspiration for achieving controlled ion flow in artificial ion channels historically came from biophysics. Here, we instead draw the initial inspiration from the chemistry of complex formation between crown ether molecules and dissolved metal ions to demonstrate strain-gated permeation across locally suspended sub-nanoporous graphene and hexagonal molybdenum disulfide (MoS₂) monolayers. Using extensive all-atom molecular dynamics simulations informed by density functional theory calculations, we investigate electrostatically driven aqueous ion permeation across precisely engineered sub-nanometer pores in two-dimensional (2D) membranes under the influence of tensile strain.

In graphene, highly strain-sensitive solid-state ion channels are achieved via membrane-embedded crown ether pores, which exhibit trapping of certain aqueous cation species in the pores due to ion-crown complexation at room temperature. The resulting highly mechanosensitive permeation of potassium ions is shown to arise from a strain-controlled competition between ion-crown and ion-solvent interactions, enabled by the atomic thinness of graphene [1]. Additionally, ion trapping in crown-porous graphene is demonstrated to enable strain-controlled sieving of salt mixtures. In MoS₂ monolayers, mechanosensitive sub-nanopores selective to either anions or cations can be achieved by precise multivacancy engineering, in principle not requiring additional chemical functionalization of the pore lining, because MoS₂ contains two atom species with significantly different electronegativities and thus considerable partial electrostatic charges. The high strain sensitivity in ion permeation across sub-nanoporous MoS₂ membranes is shown to arise from the reduction of ion-pore repulsive interactions upon pore dilation caused by lattice strain. For both graphene and MoS₂-based membranes, current modulation at the order-of-magnitude level per a few percent of lattice strain is demonstrated. Pore structures similar to those considered here have been reported experimentally and thus our results potentially lay ground for a new class of solid-state membranes with ion permeation properties sensitively controlled by externally applied tensile lattice strain.

References
Effect of Inhomogeneous Nanoscale Strain on Monolayer Tungsten Transition Metal Dichalcogenides Investigated by Nano-Photoluminescence Spectroscopy and Nano-Raman Scattering

Two-dimensional materials suitable for targeted missions with limited resources. Two dimensional material-based environmental sensors can be used for the

Multifunctional Sensor Platforms made of Two Dimensional Materials

Two dimensional materials offer a unique set of advantages as sensors for space applications. For instance, two dimensional materials such as graphene and molybdenum disulfide have high surface-to-volume ratio and low Johnson noise, resulting in highly sensitive gas sensors. In addition, great mechanical, thermal, and electrical stability, as well as radiation hardness due to minute cross-sectional area, make them useful in space applications. Furthermore, lightweight, low power consumption and small size make the two dimensional materials suitable for targeted missions with limited resources. Two dimensional material-based environmental sensors can be used for the *in situ* detection of neutrals, trace gases, volatile organics and environmental parameters in a number of disciplines, including Planetary Science, Earth Science and Heliophysics. For example, these nanosensors can detect gases that can fingerprint various biological and abiotic processes on outer planetary bodies. They can be used to simultaneously detect methane, ammonia and other gases difficult to detect using mass spectrometry due to mass interference issues, and thus can be used in tandem with mass spectrometers. In addition, these miniaturized sensors can be used for quick screening of samples in sample return missions without adding significantly to the mass and power of the payload. Furthermore, Human exploration missions can benefit from these highly sensitive sensors to detect leaks of toxic gases that are commonly onboard such as hydrazine, ensuring human safety and mission success. In this talk, we will discuss our work on developing a multifunctional sensor platform with a suite of environmental sensors fabricated with a variety of nanomaterials.

Making Use of Nano-Bubbles and Nano-Tents Formed by 2D Materials

Nanobubbles at room temperature. This extreme effect of nanobubble strain on both the Raman and photoluminescence signals shows dramatic heterogeneity over the nanobubbles. For both WSe$_2$ and WS$_2$, TEPL and TERS signals show large enhancement with increasing strain from the nanobubble. Additionally, longer wavelength bound exciton luminescence is observed in both WSe$_2$ and WS$_2$ nanobubbles at room temperature. This extreme effect of nanobubble strain on both the Raman scattering and photoluminescence shows the promise of using nanobubble strain to engineer the properties of excitons in monolayer TMDs for novel opto-electronic applications.
QN03.10.01

Two-dimensional (2D) materials provide a wide range of unique properties that enable light generation, modulation, and detection for photonic applications, and could offer an alternative solution for heterogeneous integration by the advent of sufficiently strong van der Waals (vdW) force combined with mature and low-cost CMOS fabrication technology [1]. Hence, it is important to understand the interaction of 2D materials with Silicon photonic platform since their real vs. imaginary part of the optical indices decay away from the exciton resonance have different impacts on the telecom-operating photonic structures [2]. In order to achieve, a detailed understanding of the loss and index change on Si photonics, as per example, the precise and cross-contamination free transfer of 2D materials is essential. In reality, the state-of-the-art of TMDs transfer techniques are not benign with taped-out chip technology due to the inability to place a single 2D material flake on the pre-fabricated photonic chip without incurring significant cross-contamination (e.g. transfer of undesired flakes). We recently provided a solution for this challenge developing a 2D material printer enabling cross-contamination-free transfers without impacting the underlying photonic waveguide structures [3,4]. Finally, we discuss our latest results on passive coupling tunability and index determination using a semi-empirical approach with heterogeneously integrating TMDs layer on Si micro-ring resonator for broadband-on-chip modulators and photodetectors with high-speed and high responsivity [5].

Our results indicate that 2D materials could be an essential building block for a fully integrated photonic circuit.

References

QN03.10.02
Large Single-Crystals Synthesis WSe2 Monolayer by Chemical Vapor Deposition Zhenfeng Zhang, Xiaole Xu, Jian Song, Yubao Zhang, Xuefei Li and Yanqing Wu; Wuhan National High Magnetic Field Center and School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, China.

The rich and diverse physics with novel electrical transport and optical properties of transition metal dichalcogenides (TMDs) offer unprecedented opportunities for electronics and optoelectronics applications. However, CVD growth of large-area TMDs film with high mobility is still a challenge. Here, we present an approach for growing monolayer WSe2 with high quality on c-plane sapphire substrate using a low pressure chemical vapor deposition (LPCVD) method. We can successfully obtain WSe2 monolayer with single domain size up to 144 μm in 15 minutes with clean and regular triangle morphology. This synthesis approach of high-quality large domain size of 2D TMDs film provides a pathway for high-performance 2D electronic devices.

QN03.10.03
The Route Toward Graphene-Metal Composites Kaihao Zhang and Sameh Tawfick; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

The pursuit of high quality multifunctional carbon-based composite materials is driven by a myriad of application lined-up for strongest synthetic structure ever produced. There have been extensive studies, over the past decades, incorporating low-dimensional materials such as carbon nanotube and graphene in metal matrix, whereas no rational design route of graphene-metal composites has been elucidated due to the lack of understanding of graphene-metal interacting at multiple length scales. To gain insights in graphene-metal interactions and to build a rational design route of strong graphene-based macroscopic assemblies and composites, we use a model system incorporating high quality monolayer graphene in single crystalline ultra-thin metal matrix via rapid chemical vapor deposition (CVD) processes.

The ultra-thin metal matrix having thickness less than 200 nm has been manufactured by beating and used extensively for gilding sculptures, precious furniture and building exteriors for over 3000 years. Palladium (Pd) leaf is used as a gilding material for its silver color and excellent anti-corrosion properties. We choose Pd leaf as the metal matrix for two additional reasons: (i) its high carbon solubility at elevated temperatures (~150-fold higher than that of copper at 1000 C). This helps to achieve high carbon segregation flux for graphene nucleation. And (ii) its high binding energy with graphene layer (~2.5-fold higher than that of copper). Graphene-metal interaction gives rich insights of strengthening/toughening mechanisms of graphene in macroscopic composites. In this work, the Pd leaf catalyst is made by hammer beating of a micrometer thick foil. During this process, Pd thickness is reduced to 150 nm while the average grain size exceeds 20 μm. The Pd leaves made by high strain rate beating are stable at synthesis temperature up to 1100 C for 30 s, resisting solid state dewetting owing to their extremely low grain triple junctions density (~ 0.017 μm-2). Mathematical models of low pressure CVD synthesis kinetics on ultrathin metal catalysts guide the development of extremely rapid graphene synthesis conditions, resulting in the formation of high quality uniform graphene monolayer on thin Pd films in less than one minute. Graphene grows rate is twice as fast as copper-catalyzed growth. Uniaxial strain testing with Raman spectroscopy reveals the excellent crystallinity of graphene by probing the stress-induced phonon shifts.

Notable enhancement in mechanical properties is observed in the as-grown Pd-Gr thin film composites. The pristine Pd leaves can be readily transferred to a slotted transmission electron microscopy (TEM) grid, then shaped into doubly-clamped freestanding strips via focused ion beam (FIB). We dope the Pd strip surface with monolayer graphene via the proposed rapid CVD synthesis. Using nanoindentation with a wedge indenter on the Pd-Gr strips, we demonstrate the graphene’s ability to significantly stiffen the Pd leaves by over 116 %. Moreover, indentation, activation and unloading on the nanostructured Pd-Gr strip enables the fracture toughness measurement of ultra-thin film materials. The Pd-Gr exhibits 289.5 J/m² fracture energy, which is over 3.7-fold of the pristine Pd. This new graphene-metal composite material could open exciting opportunities in harnessing superb properties of 2D materials.

QN03.10.04
Facile Fabrication of Freestanding Size Tunable Graphene Nanomesh for Plasmonics Vivek Garde1, 2, 3, Rakesh Motel2 and Jing Fu3; 1IITB Monash Research Academy, Mumbai, India; 2Indian Institute of Technology Bombay, Mumbai, India; 3Monash University, Melbourne, Victoria, Australia.

Graphene, owing to its excellent electron transport together with a high mechanical strength, has opened up a new pathway in electronics since its discovery. Device applications of graphene, owing to its zero band gap, however, have been limited, and significant efforts have been made to introduce a band gap by including defects in pristine graphene. Patterned graphene is also employed and graphene nanoribbons (GNR), quantum dots (GQD), nanomesh (GNM), etc. have been used for band gap opening and transform graphene from semi-metal to semi-conductor for potential applications in visible to infrared plasmonics. A sizeable band gap can be engineered based on quantum confinement induced by patterned graphene, making the patterning of graphene an important research area.

Lithographic techniques along with plasma etching are most commonly used for graphene nanopatterning. However, referring to the violent nature of plasma etching, graphene nanopatterning inaccuracies. The key challenges are precision, size tunability, high periodicity avoiding the lateral damage in nanopatterning.

In this work, a facile and systematic approach for graphene nanopatterning with ion beam is presented, and size tunable graphene nanomesh on a suspended single layer graphene is shown. The beam overlap function and step size in a gallium FIB are used for nanomesh fabrication with tunable size (30-100 nm) and period (50-100 nm). The fidelity of FIB milling for graphene patterning is demonstrated and revealed by SEM, TEM and AFM imaging. The effect of fabrication parameters is evaluated and graphene cutting conditions are optimized, in addition to patterning. This is important from a technological perspective and graphene device applications. Fabricated nanomesh is size tunable, offering...
potential graphene plasmonics applications. The versatile nature of proposed approach avoiding lateral damage for graphene nanopatterning allows flexibility, and we also demonstrate the fabrication of size tunable graphene nanoribbons. Gold-graphene nanomesh, based on the developed graphene nanopatterning approach, is further presented and illustrated for graphene plasmonics and optical modulation of visible light. The plasmonic response, calculated with finite-difference time-domain (FDTD) electromagnetic simulations, offered through composite graphene-gold nanomesh architecture is in the visible range, and is tunable through the geometrical parameters, providing an opportunity for FIB nanopatterning for graphene plasmonics. Gold-graphene nanomesh offers field enhancements through patterned nanomesh, which arises from localized surface plasmons at the nanostructures significantly, improve the performance of graphene plasmonic devices. In summary, a nanopatterning approach for freestanding size tunable single layer graphene nanomesh is developed and graphene plasmonics is further illustrated through the development of composite graphene-gold nanomesh for optical modulation in the visible spectrum. The demonstrated approach shows endeavour for graphene patterning and future applications of graphene for plasmonics, gas sensing, water desalination etc. with just one processing step.

**References:**


**To study the Role of Dimensional Variation in Molybdenum Disulphide (MoS\(_2\)) by Relating the Morphological, Structural and Optical Characteristics**

Molybdenum disulphide (MoS\(_2\)) as a transition metal dichalcogenides (TMDs) sketching a wide research interests with unique optical and electronic properties then a bulk. Bandgap engineering technique is a potential way for tuning to its optimization. MoS\(_2\) owing to band gap tailoring from 1.3 to 1.9 eV for bulk (indirect) and single-layered (direct) structures makes it a promising material in the field of energy applications. The present article deals with variation in the properties along with dimensional (1-3D) change in molybdenum disulphide nanostructure. Synthesises, structural, morphological, optical properties of bulk to few layers of nanostructures are investigated. The exfoliation of MoS\(_2\) flake like nanostructure has been studied for its unique properties. Uniform 3D flower like nanostructures has been prepared by one-pot hydrothermal method. Nanostructure flakes by a solution based exfoliation method are compared with a bulk MoS\(_2\). Structural, morphological and optical properties were investigated by XRD, FESEM, EDAX, UV–Visible for the bulk and nanomaterials properties.

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Molybdenum disulphide (MoS\(_2\)) as a transition metal dichalcogenides (TMDs) sketching a wide research interests with unique optical and electronic properties then a bulk. Bandgap engineering technique is a potential way for tuning to its optimization. MoS\(_2\) owing to band gap tailoring from 1.3 to 1.9 eV for bulk (indirect) and single-layered (direct) structures makes it a promising material in the field of energy applications. The present article deals with variation in the properties along with dimensional (1-3D) change in molybdenum disulphide nanostructure. Synthesises, structural, morphological, optical properties of bulk to few layers of nanostructures are investigated. The exfoliation of MoS\(_2\) flake like nanostructure has been studied for its unique properties. Uniform 3D flower like nanostructures has been prepared by one-pot hydrothermal method. Nanostructure flakes by a solution based exfoliation method are compared with a bulk MoS\(_2\). Structural, morphological and optical properties were investigated by XRD, FESEM, EDAX, UV–Visible for the bulk and nanomaterials properties.
Two dimensional (2D) layered materials are widely studied due to the exceptional physical properties they exhibit compared to bulk, with a promise to add new functionalities to the existing nanoelectronic devices. It is important to realize low resistance contacts to these 2D semiconducting materials for high performance devices without degrading the pristine quality of the underlying 2D semiconductor. This is difficult to achieve with conventional metal contact schemes. 2D layered metals fall in a less explored class of materials and are ideal candidates for contacting layers to semiconducting 2D layers as they create less defects on other 2D materials due to the innate layered structure. 2H-TaSe$_2$ is one such layered 2D metal that shows simultaneously strong electron-phonon coupling and spin-orbit coupling, which play a crucial role in charge density wave (CDW) driven transport properties [1-2]. It exhibits the highest CDW transition temperature among 2H TMDCs. Interestingly, there is a large gap above and below the bands around the Fermi energy in the normal metal phase of TaSe$_2$ and is expected to possess interesting optical properties, which remain largely unexplored[3]. We exploit this bandstructure in this work to show that due to inter-band transitions, TaSe$_2$ shows strong optical absorption and photoluminescence with a tunable peak position by changing the temperature and thickness of the flake. The perfect combination of excellent electrical transport and optical properties makes 2H-TaSe$_2$ a unique material for flexible, “all-2D” optoelectronic applications. In this context, we show several device applications of TaSe$_2$ in this work, demonstrating its versatile usage as nano-opto-electronic material, as discussed below.

(1) We show that TaSe$_2$ can be used as an efficient donor layer for non-radiative resonant energy transfer (NRET) to other semiconducting layered material[4], allowing us to enhance the photoluminescence intensity of multilayer - stack 2H-TaSe$_2$ heterojunction device, we have used an efficient hot electron injector with large carrier diffusion length (unlike conventional metals), (2) We demonstrate TaSe$_2$ as an efficient contact material for planar and vertical heterojunction devices. (3) Finally, we demonstrate a gated TaSe$_2$/MoS$_2$/graphene vertical junction for photodetection applications where TaSe$_2$ is used as a dual-purpose layer, namely as light absorber and as photocarrier collector. The photodetector exhibits a responsivity of 10 A/W with an operating speed of 0.1 MHz. The results will ignite studies on several device explorations of TaSe$_2$ in nanoelectronic and optoelectronic domain.

References:

QNO3.10.10

Electrical Properties of Quasi 1D Germanium Selenide (GeSe) Nanoflake Field-Effect Transistors

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We report on the electrical properties of natural quasi 1D p-type GeSe nanoflakes, which were mechanically exfoliated from GeSe single crystals by the polydimethylsiloxane (PDMS) stamp method, using a back-gate field effect transistor (FET) measured in a vacuum probe station at room temperature. In this study, we used two contact metals, including Au and Cr metals, as the Ohmic contacts to the GeSe nanoflake FETs, resulting in an Ohmic behavior with the Au contacts, with a total resistance of 5.5×10$^4$ Ω. We also found that the 40-nm-thick GeSe nanoflake FET exhibits clear p-type semiconductor behavior with a field-effect mobility of ~1.0×10$^4$(cm$^2$/Vs) and a current on/off ratio of ~10$^4$ at 4K.

QNO3.10.11

Giant Photoluminescence Enhancement Through Non-Radiative Energy Transfer in 2D/2D Heterostructure

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The photoluminescence (PL) emerging from monolayer transition metal dichalcogenides (TMD) with their direct bang gap nature [1] and high binding energies of excitons [2] is prospective for multitude of nanoscale optoelectronic applications. However, the impeded amount of light absorption imposed by the monolayer thickness impedes the realization of viable TMD based optoelectronic devices. Using a van der Waals (vdW) heterostructure of monolayer MoS$_2$stacked on top of multilayer SnSe$_2$, we demonstrate PL enhancement of MoS$_2$ by more than an order of magnitude over the entire overlap area. Counteracting the PL quenching from ultrafast charge transfer across the highly staggered conduction bands of MoS$_2$ and SnSe$_2$, PL of MoS$_2$ enhances by 14x with 633 nm excitation and 5x with 532 nm excitation at room temperature. Similar enhancement is observed with monolayer WS$_2$ stacked on multilayer SnSe$_2$. The enhancement factor is found to be a strong function of the thickness of SnSe$_2$ flake. The PL enhancement retains up to 5x even with the insertion of hBN as thick as 10 nm across MoS$_2$ and SnSe$_2$.

This kind of robust enhancement is facilitated through sensitization of PL of TMD by strongly resonant dipole-dipole coupled energy transfer [3] to monolayer TMD from SnSe$_2$ which acts as a scavenger of light unabsorbed by the monolayer. Multilayer SnSe$_2$ has a strong optical absorption with a direct bandgap of about 2 eV [4] that closely matches with $A_\text{h}$, exciton state energy in MoS$_2$ or WS$_2$. These kind of layered heterostructures are lucrative for exploiting the energy transfer mechanism because of efficient dipole-dipole coupling at the closest possible spaced in-plane dipoles that match in momentum and delay conservation enabled by energy transfer from free electron-hole pairs to highly luminescent $A_\text{h}$ exciton states. At low temperatures (from 200 K to 4 K), we observe a quenching of the PL instead of enhancement, due to suppression of SnSe$_2$ absorption upon reducing temperature. Quenching is also observed when the donor material is replaced from SnSe$_2$ to a weakly absorbing material like TaS$_2$ [5]. The mechanism is further confirmed by polarization resolved PL data and the effect of different parameters on the factor of PL enhancement is analyzed upon constructing a microscopic energy transfer model. Such large area, uniform, highly efficient photoluminescence enhancement through non-radiative energy transfer is promising for the design of optoelectronic devices with layered materials.

References:

QNO3.10.12

Role of Surface Induced Defect States on Thermoelectric Power Factor in MoS$_2$

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Two-dimensional materials such as MoS$_2$ have been show to exhibit large Seebeck coefficient and are promising candidates for thermoelectric energy conversion [1]. The ab-initio calculations predict a high intrinsic thermoelectric power factor if the substrate effects are excluded [2]. But the overall power factor is typically limited by its low electrical conductivity. This is possibly due to localized states arising from the impurities and the adsorbates introduced from the substrate [2]. In this work, we measure Seebeck coefficient and electrical conductance of CVD grown MoS$_2$ flakes on Si/SiO$_2$ substrates [3]. We observe hopping transport from the localized states introduced by the substrate at low temperatures and low electrostatic doping. To reduce the observed defect states, we use 2D hexagonal boron nitride (hBN) as a substrate because it provides less charge inhomogeneity and atomically flat surface. The CVD grown MoS$_2$ monolayer is placed on top of hBN using a dry transfer printing process and a PDMS stamp [4]. We observe an enhanced thermoelectric power factor of from MoS$_2$ on hBN substrate over Si/SiO$_2$. However, we still find the localized states to be dominating the extended states from Seebeck measurements at low temperatures and high doping. We attribute these defect states observed in hBN/MoS$_2$ to arise from the dry transfer printing process that could introduce strain heterogeneity. We systematically characterize the defect states through electrical measurements and similarly transfer printed monolayer MoS$_2$ on Si/SiO$_2$ substrates. This work advances the understanding of substrate effects on transfer printed 2D materials for improved thermoelectric performance.

Graphene is a 2D allotrope of carbon with fascinating chemical and physical properties. Its unique electronic structure and surface sensitivity qualify this single layer of sp²-carbon atoms as a promising material for sensor applications in the form of field-effect devices. As descendants of the ion selective field-effect transistor (FET), graphene FETs have been developed in the past years as part of the future of sensing devices. During measurements, the Dirac point of graphene is tracked. Stuiklin on the surface of graphene influence the position of this point of minimal conductivity. Examples for this effect range from graphene’s pH-sensitivity [1], over charge transfer doping effects e.g. by gas molecules [2], to the detection of biomolecules based on changes in the electrostatic charge distribution on the surface [3]. Using covalent chemical functionalization the physical properties and selectivity of graphene can be tuned to realize selective sensor surfaces.[4] In this work, we focus on non-covalent interactions between redox active molecules and graphene.

Graphene has been applied as an electrode material as well. Being used as a working electrode in electrochemical studies, it shows high electron transfer rates for canonical redox couples such as [Fe(CN)₆]³⁻/⁴⁻.[5] The Marcus-Gerischer theory can be applied to describes the electron transfer between a redox active species and an electrode. Therein, the position of the occupied or unoccupied states of the redox active species relative to the electronic structure of the electrode material plays a key role. Due to its unique electronic structure, graphene is particularly interesting in this context being neither metal nor semiconductor, which separates it from other 2D materials beyond graphene. The Marcus-Gerischer theory has been successfully used to explain charge transfer doping of graphene by the O₂/H₂O redox couple.[6]

In this study, we have investigated the interfacial interactions of redox active molecules with graphene, based on measurements using electrochemically grafted graphene FETs and cyclic voltammetry. [Fe(CN)₆]³⁻/⁴⁻ was used as the main probe. The influence of different factors was tested including the pH of the electrolyte solution, the initial oxidation state of the probe as well as the position of the standard potential of the redox couple with respect to the Dirac point. We showed that, while the electrochemical activity is independent of the initial oxidation state of the redox-couple, only the oxidized form [Fe(CN)₆]³⁻ exhibits charge transfer doping onto graphene. In this presentation, we explore systematically the influence of several factors on the observed doping effect.

References:

QN03.10.14
Light Emitting Devices Based on van der Waals Heterostructures with Plasmonic Nanocavities
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Van der Waals heterostructures have recently emerged as promising materials for a new generation of optoelectronic devices. Due to dangling-bond-free surface of 2D materials, the constraints of lattice matching are lifted giving unprecedent flexibility for the device fabrication. Van der Waals heterostructures comprising semiconducting 2D layers are of particular importance, since monolayer materials, for example MoS₂ and WS₂ can be direct bandgap semiconductors in contrast to their bulk counterparts. Various van der Waals heterostructures have been explored for electrically induced light emission, where proof-of-principle devices were typically made of exfoliated materials drastically limiting reproducibility and scalability. Consequently, for practical device applications, large scale materials grown by chemical vapour deposition (CVD) technique are crucial. In this work, we study electrically induced light emission in vertical van der Waals heterostructures fully produced from CVD materials. Vertical graphene contacts are employed to facilitate efficient injection of both the electrons and holes in the active materials such as WS₂. Using hBN tunneling barriers between graphene contacts and active semiconductor materials, the current leakage is minimized for efficient electron-to-photon conversion. Next, the van der Waals heterostructures are combined with plasmonic nanocavities to enhance light emission efficiency and control emission spectrum.

References:

QN03.10.15
Ultrafast Carrier Dynamics in Few Layer Colloidal Molybdenum Disulfide Probed by Broadband Transient Absorption Spectroscopy
Pieter Schiettecatte, Pieter Geiregat and Zeger Hens; Ghent University, Gent, Belgium.

Ultrathin two-dimensional (2D) group VI transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS₂) have attracted much attention in opto-electronics due to their extraordinary properties. As bulk materials, they feature a layered crystal structure consisting of stacked monolayers weakly bound by Van der Waals interactions. The combination of these weak out-of-plane forces with strong in-plane chemical bonds enable ultrathin mono-and few-layered TMDs to be produced using top-down exfoliation methods, vacuum deposition approaches and, more recently, solution-based wet-chemistry methods. Vacuum deposition approaches have arisen as key methods to produce large area monolayer films, yet their high cost and substrate dependence, still remain critical concerns. In this respect could colloidal synthesis offer an inexpensive and scalable alternative as the production and processing of materials in solution opens ample possibilities for large-area device fabrication with a high degree of tunability. [1]

Over the past years, much work has been devoted to understanding photophysical processes occurring in MoS₂ flakes made by exfoliation or CVD. Using a series of spectroscopic techniques it was shown that their physics is being largely governed by enhanced many-body Coulomb interactions which result from quantum confinement and reduced screening. [2] These effects have shown to give rise to pronounced exciton binding energy and band gap renormalization effects. Such studies have not only contributed to a broader fundamental knowledge but were also pivotal for advancing the use of MoS₂ in a broad range of applications. To date, few, if any, studies have addressed the photophysical properties of MoS₂ produced by colloidal synthesis. An overview study is therefore relevant and timely as these materials are produced through an entirely different chemistry - low temperature solution phase versus high temperature gas phase (cf. CVD) and bottom-up versus top-down (cf. exfoliation). In addition would the knowledge obtained in this study undoubtedly pave the way for a more rational fine-tuning of emerging synthetic protocols.

In this contribution, we address the relaxation dynamics of few layer colloidal MoS₂ sheets after photoexcitation by means of femtosecond transient absorption (TA) spectroscopy at visible and near infrared wavelengths. We show that the transient absorbance after photoexcitation results from the joint effect of (a) a reduced oscillator strength of the so-called A and B exciton and (b) a redshift of the entire absorbance spectrum; features we assign to state filling and band-gap renormalization, respectively. Both components exhibit a close to first order decay, yet their rate constants differ markedly. All signatures of state filling disappear from the transient absorbance at a rate of 4 ps⁻¹. In line with the work by Cunningham et al. [3], we attribute the loss of state filling to the trapping of charge carriers - electrons in this case - in midgap states. The bandgap renormalization decays at a rate of 0.1 ps⁻¹, which reflects the rate of the eventual non-radiative charge-carrier recombination. Although being made by an entirely different chemistry, colloidal MoS₂ nanosheets have shown a great resemblance to the state-of-art CVD grown flakes. These results are promising for the future development of colloidal TMDs and their rational fine-tuning according to state-of-the-art post-treatment techniques which would undoubtedly pave the way for their incorporation in device applications.

Passivation of Black Phosphorus using Plasma-Enhanced Atomic Layer Deposition High-k Dielectrics Katherine Price1, 2, Sina Najmaei2, Madan Dubey2 and Aaron D. Franklin1
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The growing research interest in black phosphorus (BP) as a remarkable material with applications in electronics and optoelectronics has made the study and development of device fabrication and integration processes an essential research area. Specifically, the weak material integrity and oxidation chemistry of BP makes the development of robust passivation techniques vital to preventing degradation in BP. The rapid interactions of BP with O and H2O in air leads to formation of oxides and quick degradation of its electrical and optical properties. An approach, compatible with electronic and optoelectronic device fabrication, that can protect and preserve BP properties is the dielectric capping of the 2D crystal. In this work we will explore and develop scalable (~10 nm) processes for deposition of high-k dielectrics as capping layers on BP using plasma-enhanced atomic layer (PEALD). We demonstrate how the high energy chemical processes and minor defect formations at the interfaces in the PEALD process can enhance the nucleation of the high-k dielectrics on the surfaces of the BP to enable high quality thin film deposition. We are currently developing carrier-selective Schottky-type photovoltaic devices that utilize this new high performance BP capping layer and will fabricate photodetectors with external quantum efficiency up to 0.2% that show good uniformity and homogeneity over multiple layers.
Anomalous Valley-Selective Optical Stark Effect in Monolayer WS

Converse flexoelectricity induces mechanical stress under an inhomogeneous electric field in all dielectrics. Although this electromechanical behavior has great potential as an efficient and low-cost electronics, including solar cells, touchscreens, displays, and printed electronics. So far, there have been several thin film materials with such potentials, such as graphene-like state, known as reduced graphene oxide (rGO). Subsequently, GO is treated in reducing condition to remove oxygen containing functional groups gained during the oxidation, thus, reverting it back to graphene-like state, known as reduced graphene oxide (rGO).

Valley pseudo-spin and broken inversion symmetry leads to valley-specific optical selection rules in monolayer transition metal dichalcogenides (TMDC). Specifically, the degenerate K and K' valleys can be selectively populated with right- and left-hand circularly polarized light. This control of the band edge states has fueled interest in the potential of TMDCs for Valleytronics applications, where the momentum state is manipulated to perform computational and/or logical operations.

Recently, it was discovered that intense circularly polarized light fields can be used to break the degeneracy between the K and K' valley, allowing the energy levels of each valley to be independently tuned via a valley-selective form of the well-known optical Stark effect\(^1\)\(^2\) and lesser-known Bloch-Siegert\(^2\) effects. For high-intensity sub-resonant illumination with right-hand circularly polarized light, the K-valley A-exciton absorption band will blue-shift to higher energies. In the past, this has been described by the dressed-atom picture, which predicts that the effect reverses to a red-shift for above-resonant illumination. Additionally, application of Floquet theory to describe those observations has led to the prediction of topologically protected chiral edge states for above-resonant light fields. We do not see a Stark shift associated with intervalley biexcitons.

We do not see a Stark shift observed for the opposite (i.e. K') valley, confirming the valley-selective nature of the optical Stark effect in TMDCs. For near-resonant pumping of the K-valley, no Stark shift is observed for the opposite (i.e. K') valley, confirming the valley-selective nature of the optical Stark effect in TMDCs. For low-dimensional semiconductors, we suggest that exciton-exciton repulsion needs to accounted for to predict the near-resonance behavior of the optical Stark effect. Our results may have implications in the search for topologically protected chiral states in TMDCs.

References

Converse Flexoelectric MoS\(_2\) Thin-Film Actuator

Converse flexoelectricity induces mechanical stress under an inhomogeneous electric field in all dielectrics. Although this electromechanical behavior has great potential as an actuation mechanism, flexoelectric actuators have not been widely studied, which is mainly attributed to the fact that the effect of flexoelectricity is considerably small in general bulk dielectrics. Two-dimensional (2D) materials can be a practical candidate as an active material due to the scaling effect of flexoelectricity. Here, we report a molybdenum disulfide (MoS\(_2\)) thin-film actuator driven by the converse flexoelectric effect under electric field gradient. To fabricate an actuator device, single-layer chemical vapor deposition (CVD)-grown MoS\(_2\) was transferred on the substrate with an insulator on the bottom electrode, followed by comb-shaped top electrode deposition for the electric field gradient through fringe fields. To characterize the actuators, we measured out-of-plane displacements at the first harmonic resonance frequency of the input AC signal using a laser vibrometer. When we characterized the actuation performance, we measured the displacement relative to the active layer thickness of our MoS\(_2\) actuator showed more than an order of magnitude higher performance compared to other existing flexoelectric actuators. In addition, in a cyclic test, the MoS\(_2\) device exhibited consistent performance after 10\(^8\) cycles of actuation, which suggests stable operation in air conditions. The converse flexoelectricity combined with distinct properties of 2D materials will open up unique opportunities in the field of nanoelectromechanical systems (NEMS).
Non-destructive inspection of features or materials buried beneath dielectrics is highly sought after for diagnostics of micro- and nanoelectronics, and is a long lasting technical challenge. Optical microscopy allows for imaging beneath an insulator, while its lateral resolution is limited to the micron scale. Scanning electron microscopy offers sub-nanometer resolution, but often encounters sample charging obscuring the analysis of insulators. Using photoemission electron microscopy with deep-ultraviolet (deep-UV) photocathode, we show sub-surface imaging of MoS$_2$ flakes sandwiched between dielectric overlayers (up to 100 nm-thick) and an underlying SiO$_2$ films. Comparison of photomission yield to modelled optical absorption of dielectric stacks demonstrated that optical standing waves contribute to the sub-surface imaging mechanism. The presence of atomically-thin MoS$_2$ flakes modulates the optical properties of the dielectric stack locally, producing image contrasts of the buried MoS$_2$ with submicron lateral sensitivity. The results presented here underscore the role of optical effects in enhancing the depth sensitivity of photoemission images produced using low-energy photons. The benefit of this approach includes non-destructive imaging of buried interfaces and sub-surface features useful for analysis of microelectronics circuit and of nanomaterial integration into electronic devices.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). M. B. was supported by the CINT postdoctoral program. T. O. was supported by the CINT program and Sandia LDRD. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-NA0003525. The views expressed in the article do not necessarily represent the views of the US DOE or the US Government.

Study of the Electrical Disorder Sources in Transferred CVD Graphene

Electrical disorder in CVD (chemical vapor deposition) graphene limits its performance in many applications [1, 2]. Recent works on graphene sensing applications have shown that disorder induces uncertainties in the reading of Dirac voltage, which undermines their sensitivity [3]. However, the sources of electrical disorder have not been thoroughly understood yet in literature. This work presents a comprehensive study of the sources of disorder in CVD graphene. Utilizing Raman spectroscopy mapping and atomic force spectroscopy (AFM), we correlated the carrier concentration distribution [4] of transferred CVD graphene to its topographic image. The results show that due to the embedded ripple structure, which originates from the thermal expansion coefficient mismatch against the growth substrate, graphene forms uneven separation to SiO$_2$ substrate according to the ripple array. Consequently, the hole doping received from SiO$_2$ [5] alternates in a periodical manner. Further, we bisected the mapping data of graphene according to its ripple structure into valley (topographically lower) and peak (elevated by ripples) groups, and show that valley region is more disordered. Such additional disorder is from the enhanced charge interaction with the impurities in the substrate [6]. The results suggest that the disorder in graphene depends on the morphology of the ripple array, which is eventually determined by the degree of mismatch between the graphene and the growth substrate [7]. Finally, we performed AFM and Raman spectroscopy mapping on the same sample after rapid thermal annealing (RTA). The results indicate that annealing heals the size unevenness from ripple, and therefore alleviates the non-uniformity in doping distribution across the sample. However, as thermal annealing relocates graphene closer to the substrate [8, 9], graphene suffers more disorder from SiO$_2$. This study suggests that ripple is essentially not a disorder source, whereas it contributes to disorder when there is substrate doping. The authors acknowledge funding from Boston Scientific Corporation.

Unique Stacking Configurations in Bilayer Ribbons Grown on Monolayer Grain Boundaries by Chemical Vapor Deposition

Stacking orientation of atomically-thin 2D layers may serve as an interesting way to tune their optical and electronic properties for optoelectronic applications. However, it is a challenge to engineer it in a desirable way. Here, we demonstrate a synthetic strategy to enable the growth of bilayer crystals exhibiting a wide range of stacking configurations. Detailed second harmonic generation (SHG), low-frequency Raman spectroscopy, and atomic-resolution scanning transmission electron microscopy (STEM) studies of bilayer WS$_2$ ribbons are performed to reveal that the defects on the grain boundaries facilitate the growth of bilayers with a wide range of stacking angles. First-principles calculations proposed possible mechanisms of the orientationally arrangement of bilayers. We also show that the low-frequency Raman serves as a distinct signature for fast differentiation of new stacking configurations. Our finding shows a promising way to direct synthesis of bilayer crystals with weak interlayer coupling and specific mutual monolayer orientations, which is important for their future optoelectronic applications.

2D Electrides and Their Use in Atomically Thin Heterostructures

The properties of 2D materials motivate the exploration of new atomically thin materials. One class of 2D materials, demonstrated experimentally, is 2D electrides, which consist of a layer of atoms and layers of electrons on the surface. The layers of electrons are delocalized into layers of 2D electron gas. As a result, 2D electrides, such as 2D Ca$_3$N$_2$, have exciting properties like high electrical mobility, high carrier concentrations, and ultra-low work functions. To synthesize 2D Ca$_3$N$_2$, we exfoliated the layered bulk crystal Ca$_3$N$_2$ in appropriate organic solvents to shear few-layer sheets. Careful study using X-ray diffraction and transmission electron microscopy coupled with selected area diffraction showed that the sonicated Ca$_3$N$_2$ yielded crystalline 2D sheets. Measurements by ultraviolet photoelectron spectroscopy and UV-Vis-NIR spectroscopy confirmed that the 2D sheets retain the metallic electronic structure of the bulk and could serve as excellent transparent conducting materials. To build on this result conceptually, we performed computations using density functional theory (DFT) that suggest that the 2D electrides, when brought into contact with other 2D materials, donate massive amounts of electron density (up to 0.5 e- from formula unit of acceptor) and form quasi-covalent bonds between materials. This unique behavior constitutes a conceptually new type of heterostructure with properties distinct from either monolayer. Here we report calculations of electrode/graphene, electrode/hBN, electrode/black phosphorus, and electrode/Zr$_2$S$_2$ heterostructures. Exterinsic electron transfer from the 2D electrode to the acceptor creates a strong electrostatic attraction, which results in an interlayer distance (~2.0 Å) much smaller than traditional van der Waals distances in the case of Zr$_2$S$_2$. The high degree of electron transfer into Zr$_2$S$_2$ raises the Fermi level of Zr$_2$S$_2$, which populates its conduction band and converts the wide bandgap semiconductor into a metal. By calculating different orientations of the heterostructures, we show that the electron transfer and the interlayer distance are inherently coupled. We provide calculations of the anisotropic work function and give analysis of the electronic structure as one example of the exciting properties of this new type of heterostructure.

Fabricating Waveguide Patterns for Rapid Optoelectronic Evaluation of TMD Material Integration

The most common form of data communication in present day is via electrons shuttling through metal wires. However, this presents severe losses leading to incoherent communication for long-reach applications. Light propagating through a well-defined path, such as in a waveguide, offers the most promising future in data communication. Optical on-chip and inter-chip connections provide high-bandwidth communication in short-reach applications as well as very little losses for long-reach applications. We are to explore a broad range of 2D metal dichalcogenides and their alloys such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$, for applications as advanced opto-electronic materials. The combination
of tunable bandgap, interface-determined structure in the absence of a bulk and Fermi-level control by electrical contacts renders them a materials system with great potential for application as emitters and sensors, e.g. for on-chip and inter-chip optical communication. The high stability and facile preparation of MoS2 and related materials suggests great potential in this system, rendering them an ideal target for a research project that seeks novel materials for mastering energy and information on the nanoscale to create new technologies. We use the Molecular Foundry nanofabrication facility to fabricate on-chip waveguides out of a silicon nitride on silicon dioxide substrate including edge-couplers initially and grating-couplers that are tailored to the bandgap of common TMD materials between 1.5 and 1.9 eV. These grating couplers act as seed locations via etching and depositing specific metals, initially molybdenum, via e-beam evaporation due to its directional nature. Preliminary data utilizing waveguides with couplers at unsuitable wavelength (but within the abilities of the lithographic processes available to us) show structurally promising result, but lack functionality. Preliminary seeding growth results show monolayer MoS2 single islands on side walls. More results will be acquired using the optical wave-guide testbed system built in a nitrogen enclosed glove-box environment.

QN03.10.29 Structure and Properties of High-Mobility MoTe2, Phase Aniruma Singh1, Ryan Beams2, Irina Kalish2, Sergiy Krylyuk2 and Albert Davydov2; 1Arizona State University, Tempe, Arizona, United States; 2National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 3Food Drug and Administration, Silver Spring, District of Columbia, United States.

Recent experimental demonstration of temperature- and electric field- driven reversible phase transition of the semiconducting 2H-polymer of MoTe2 to the metallic JT- polymorph has been shown to be an appealing strategy for phase-change devices and ohmic contacts for nanoelectronics. However, several studies have reported a non-intentional loss of Te in microscopic regions of the films leading to the formation of Te-deficient phases such as MoO3[1] and MoO2[2]. In this study, we present the experimentally measured as well as density-functional theory computed Raman spectra of the MoTe2 phase to guide an unambiguous experimental identification of this Te-deficient phase. Using first-principles simulations, we also examine the structure, energetic stability, electronic and vibrational properties of MoTe2 compound and fourteen Mo-intercalated MoTe2 and MoO2 phases. We find that, unlike MoTe2, MoO2Te4 is amenable to Mo-intercalation which increases its charge-carrier mobility. [1] ACS Nano 9.6, 6548-6554 (2015); [2] Advanced Materials 29.18 (2017)

QN03.10.30 Nonvolatile Memories with Graphene Ferroelectric Field-Effect Transistors—Up-Scaling and Practicality Morteza Hassanpour Amiri and Kamal Asadi; Max-Planck Institute for Polymer Research, Mainz, Germany.

Graphene has a great promise for many opto-electronic applications. Chemical vapor deposition (CVD) of graphene is a technologically viable method for graphene production. Conventional photolithography and deposition of metal contacts on top of the transferred graphene layer to fabricate microelectronic devices is potentially invasive for graphene, and yields large spread in device parameters, and can inhibit up-scaling. In this contribution, we use an alternative process technology in which both lithography and contact deposition on top of graphene are prevented. First a pre-patterned substrate is fabricated that contains all the device layouts. Then CVD graphene is transferred on top using a conventional or laser induced forward transfer. The metal–graphene contact shows low contact resistances below 1 kΩ μm. The conformal transfer technique is scaled-up to 6” wafers with statistically similar devices, and can be applied by the transfer of any two-dimensional material. Next, we demonstrate ferroelectric field-effect transistors (GraFeFET) using the conformal transfer technique. As ferroelectric gate we use a ferroelectric polymer, poly(vinylidenefluoride-trifluoroethylene), P(VDF-TrFE). Device processing was optimized to obtain robust, highly reproducible GraFeFETs that operates at both electron and hole accumulation regimes. We present further dual-gated GraFeFETs wherein the on/off ratio can be controlled by a second nonferroelectric gate. Finally, we present a model that captures the device physics of a GraFeFETs by incorporating the polarization of the ferroelectric gate. The model predicts practicality of the graphene ferroelectric field-effect transistors, and gives criteria to improve the on/off ratio and the memory performance.

QN03.10.31 Spatially Resolved Solid-State Reduction of Graphene Oxide Thin Films Maica Morant and Kamal Asadi; Max-Planck Institute for Polymer Research, Mainz, Germany.

The current paradigms at both the industrial and research level produce reduced graphene oxide (rGO), an insulating form of graphene, only in the bulk form. For a wide range of applications, from microelectronics to water peroration, spatially resolved and controlled reduction of GO in (thin-)film is needed to reestablish electrical conductivity. Such demands require a paradigm shift in the reduction process, which should be free from intentionally used auxiliaries such as electrolytes and high temperatures. Reestablishment of the electrical conductivity in GO is (partially) obtained by reduction through high temperature treatment in a reducing atmosphere, or using strongly reducing chemicals or electrolytic processes. The reduction methods, as noted above, are suited only for bulk graphene oxide. Spatially resolved reduction of thin films of graphene oxide is important for wide range of applications such as in microelectronics, where an electrolyte-free, room temperature reduction process is still needed. In this contribution, we present spatially resolved solid-state reduction of graphene oxide thin films. We demonstrate that the reduction mechanism is based on electrolysis of water that is adsorbed on the graphene oxide thin film. The reduced graphene oxide thin-films show sheet resistance of only several kΩμm, with weak temperature dependence. Graphene oxide can be produced on a large scale and processed using low-cost solution casting techniques. Spatially resolved reestablishment of conductivity in GO can be used in electrically controlled water peroration or in micro- and nanoelectronic applications for instance as an anti-fuses.

QN03.10.32 Effects of Conductive Polymer Composite Layering on EMI Shielding During Additive Manufacturing Eugene Zakar, Theodore Anthony and Madan Dubey; U.S. Army Research Laboratory, Adelphi, Maryland, United States.

Spin coating and drop casting are viable methods for rapid and low-cost manufacturing of components for flexible devices and sensors. We investigated the cumulative effects of layering a conductive polymer mixture containing 2wt.% multiwall carbon nanotube (MWCNT) filler in a poly(3,4-ethylenedioxythiophene)poly(styrene sulfonate) (PEDOT:PSS) binder solution for application to electromagnetic interference (EMI) shielding. We determined the effects of adding solvents to the mixture, and heating for faster curing of the composite film. EMI shielding effectiveness (SE), or the measured attenuation, of the composite layers was quantified by a vector analyzer using the coaxial method in the frequency range 12-18 GHz (Ku-band).

The surface of a Mylar substrate 2mm in thickness that we used is hydrophobic in nature and does not easily wet making it difficult for any film adhesion. Rather than use traditional methods of creating hydrophilic surface by acid soaking or plasma exposure we overcame this difficulty using a simpler and more reproducible method by adding a spin coated adhesion layer of PMMA.

Drying time of the composite layer on the flexible Mylar substrate was reduced from 24 hours to 60 minutes by the addition of IPA (1:1) in the solution mixture, and further accelerated to 10 minutes with the aid of hot plate heating. Heating was optimized at 40°C for all the samples were prepared with IPA (1:1) unless stated otherwise.

RESULTS AND OBSERVATIONS: Spin coating the composite mixture yielded extremely thin films 0.05 μm, 0.15 μm, and 0.45 μm using 1x, 3x, and 9x times coating passes respectively. Their low SE of 0.1 dB, 0.25 dB, 0.5 dB were attributed to their very high film resistance of 2.5 MΩ, 25 KΩ, and 4.7 KΩ respectively. The composite stack is semi-transparent at a total thickness of 0.45 μm.

Drop-casting the composite mixture produced 10x times thicker films compared to the spin coating method. A single drop-casting produced a film 4.4 μm with a 4-point resistivity of 280 Ω·sq, and SE=5 dB. Interestingly, when we remove the IPA(1:1) which promotes faster drying of the PEDOT:PSS solution, the resistivity of the mixture reduced to 125 Ω·sq and the SE surged up to 16 dB. This seems an IPA free mixture solution yielded 3x times improvement in SE with the same thickness, due in part to the lower resistivity. A composite stacking of 4.4 μm is opaque to the naked eye.

We further examined the effects of diluting only the PEDOT:PSS component of the mixture. Drop-cast PEDOT:PSS solution has a thickness of approximately 200 nm, 250 Ω·sq resistivity and SE=12 dB. When diluted with H2O (1:1) the resistivity increased to 545 Ω·sq and SE decreased to 7.5 dB. When alternatively diluted with IPA (1:1) the resistivity increased to 415 Ω·sq but the SE decreased only slightly to 11 dB compared to the pure solution. In summary, the dilution of PEDOT:PSS solution with H2O (1:1) has a detrimental effect, in comparison to dilution with IPA (1:1) that has a subtle degradation of SE.

Drop casting 4-layers composite mixture yielded yet a greater thickness of 15 μm, with lower 63Ω/sq resistivity and higher SE=13 dB, compared to 1-layer drop-casting of 4.4 μm with SE=5dB. The SE total of 4-layers is less than the total additive effect of each layer increment. When we added two Mylar substrates with drop-casted 4-layers one top of another, a cumulative composite thickness of 30 μm (15 μm + 15 μm) was achieved that yielded an SE average ~ 17 dB. We also observed an enhanced attenuation peak of 21dB at 17 GHz, likely due to the effect from a 2mm Mylar separation absorber layer [1] formed between the two conductive polymer layers.
Sodium ion batteries are a promising more environmentally sustainable alternative to Li-ion batteries. However, the larger sized sodium ion cannot be hosted by the graphene anode material used in Li-ion batteries, and so significant research is devoted to the development of disordered carbon materials with a more open structure to serve as an alternative. One promising candidate, hard carbon, is composed of nanodomain of stacked rippled graphene.

Na intercalation into the galleries of this material is found experimentally to be energetically favorable; however, its d-spacing, while larger than graphite, is smaller than the anode material used in Li-ion batteries, and so significant research is devoted to the development of disordered carbon materials with a more open structure to serve as an alternative. One promising candidate, hard carbon, is composed of nanodomain of stacked rippled graphene.

The experimental study on the piezoelectric properties of MoS\(_2\); has shown that the cyclic stretching and releasing of MoS\(_2\) exhibits promising piezoelectric characteristics for the odd number of layers. However, the state-of-the-art relies on the mechanical exfoliation technique and its relatively small size (e.g., flakes) limits the practical adoption of MoS\(_2\) for applications requiring large-area device or system integration. In this work, we applied an unique CVD (chemical vapor deposition) technique to grow a large surface area, easy-transfer MoS\(_2\) (2cm \(\times\) 2cm) film on a SiO\(_2\) substrate, which was thoroughly characterized by using a variety of structural and electrical analysis methodologies, including Raman spectroscopy and piezoelectric testing on the flexible substrate. This work will provide a new insight on the practical application domain where the large-area, piezoelectric MoS\(_2\) can be best utilized for energy harvesting purposes.

**REFERENCES:**


**QN03.10.33**

**Disentangling the Effects of Curvature and Interlayer Spacing on Na Storage in Rippled Multilayered Graphene**

Weizi Zhang\(^1\), Wooolchul Shin\(^1\), Clement Bomnier\(^2\), Xialei (David) Ji\(^3\) and Alex Greeney\(^1\); \(^1\)Materials Science and Engineering, University of California, Riverside; Riverside, California, United States; \(^2\)Mechanical and Aerospace Engineering, Princeton University, Mechanical and Aerospace Engineering, New Jersey, United States; \(^3\)Department of Chemistry, Oregon State University, Corvallis, Oregon, United States.

Non-equilibrium synthesis and processing enables a wide variety of materials systems with tuned properties. Here we report how a prototype setup allows laser illumination to be coupled into a (scanning) transmission electron microscope (TEM) for real-time observations of non-equilibrium synthesis. The pulsed laser deposition of atomically-thin 2D materials can be performed at elevated temperatures from amorphous nanoparticles “building blocks”, and is suspected to occur by the general process known as crystallization by particle attachment (CPA). To investigate how amorphous nanoparticles of transition metal dichalcogenides (TMDs) crystallize into atomically-thin 2D layers, the process is broken into two steps. First, nanoparticles are deposited at room temperature onto TEM grids by pulsed laser deposition, and then are rapidly heated by a laser within a TEM to observe how they crystallize, fuse, and reorient into thin layers. Characterization of these “building blocks” by high-resolution electron microscopy and spectroscopy, as well as first principles modelling, is required to infer valuable information on the times scales and kinetics of the growth processes of these nanomaterials. Especially, the mobility of the nanoparticulate species on the TEM grids is highly dependent on the grid material. In addition to commercial ultrathin SiO\(_2\) grids, graphene and other 2D crystalline layers grown...
by chemical vapor deposition are utilized as platforms for synthesis, which yielded different microstructures and different kinetics. Electron energy loss spectroscopy (EELS) is utilized to understand the electronic properties and composition of synthetic 2D crystals and their heterostructures in the TEM. The observation with EELS at cryogenic temperatures with a mono-chromated TEM allows also to map with high spatial resolution the distribution of excitons. The energy of the excitons is very sensitive to the local structure and can be directly compared to photoluminescence and Raman spectra. In addition, post-growth atomic-resolution ADF-Z-STEM measurements permit the characterization of crystal phases, defects and grain boundaries at the atomic scale. These results are compared with ex situ laser annealing experiments and optical spectroscopic measurements. These nanoscale measurements to understand the growth mechanisms of crystalline 2D films from amorphous precursors should enable more rapid advancement of laser processing at the macroscale.

Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterization and computational science at CNMS were supported by the Scientific User Facilities Division, BES.

QN03.10.37
Excellent Metal-Free SERS Platforms Ruey-Chi Wang and Yu-Hsuan Chen; Department of Chemical and Materials Engineering, Kaohsiung, Taiwan.

Highly-sensitive surfaced-enhanced Raman scattering (SERS) platforms were prepared by depositing graphene oxide (GO) layers on ZnO thin films via suction filtration followed by proper heat treatments. FTIR spectra show that oxygen-containing function groups (FGs), were significantly increased after specific heat treatments. SERS measurements show that the FGs benefit enhancement factors (EFs) of SERS effects. In the work, the effects of GO thickness, heating temperature/time, and atmosphere on the FGs and SERS were investigated. Ultraviolet photoelectron spectroscopy (UPS) was employed to characterize electronic structures of the GO/ZnO composite with different heat treatments. The GO/ZnO composite annealing in Ar atmosphere at 100°C for 3h demonstrates a high EF value of exceeding 70000 for Rhodamine 6G detection. Raman mapping shows uniform intensity distribution of enhanced signals from the detection molecules. The SERS platforms show a high retention of more than 75% after aging in dark for six months. The metal-free, high-sensitive, and stable GO/ZnO composites are promising for fabricating low-cost and high-performance SERS platforms for chemical and bio-sensing.

QN03.10.38

Molybdenum disulfide (MoS2) is a kind of transition metal dichalcogenide (TMD) materials which has attracted great attention due to its various interesting properties[1][2]. MoS2 is very promising for electronic and optoelectronic devices because of indirect band gap (~1.2 eV) for few layer and direct band gap (~1.8 eV) for monolayer MoS2[3]. In MoS2 based Schottky devices, Schottky barrier height depends on the thickness of MoS2 because of its tunable electronic properties[4][5]. MoS2 have been deposited by different methods such as exfoliation, CVD, hydrothermal synthesis and other techniques. Here, we have used DC sputtering technique to fabricate metal-semiconductor junction of MoS2 with platinum (Pt) metal contacts. In this work, MoS2 thin film (~10 nm) was deposited on p-Silicon (111) using DC sputtering technique at optimized parameters. Schottky metallization of Pt metal (diameter~1mm) was also done using DC sputtering. Temperature dependent current-voltage (I-V-T) characteristics of Pt/MoS2 Schottky diodes have been investigated in the temperature range 80-300 K in the steps of 20K. Forward I-V characteristics Pt/MoS2 junction are analyzed to calculate different Schottky parameters such as Schottky barrier height, ideality factor, series resistance, Richardson constant and standard deviation. Schottky barrier height increases and ideality factor decreases on increasing the temperature from 80-300K. The I-V-T measurements suggest the presence of barrier inhomogeneities at the metal-semiconductor (Pt/MoS2) junction. Schottky barrier inhomogeneities occur if the interface is not flat or rough, then the Schottky barrier height is not remain constant and vary locally. Current transport through the junction is a temperature activated process. The electrons at low temperature pass over the lower barriers and therefore the transport will be dominated by current flowing through the patches of lower Schottky barriers and results in larger ideality factor. As the temperature increases, more and more electrons overcome the barriers and this causes the ideality factor to be close to unity and apparent temperature independent current.

References

QN03.10.39
The Evidence of Phase Transition from 1T Phase to 2H Phase of Vanadium Diselenide Dian Li, Xiong Wang and Xiaodong Cui; University of Hong Kong, Hong Kong, Hong Kong.

Vanadium diselenide (VSe2) usually exists at the 1T crystal-phase in bulk form. While the DFT calculation predicts that both 1T and 2H phase are possible stable structures at 2D limit, though 2H phase VSe2 is not reported as yet. In this work, we report the phase transition from 1T phase to 2H phase by annealing multilayer VSe2 at about 650K accompanying evidence of metal-insulator transition and Raman scattering.

QN03.10.40
Synthesis of High-Crystalline Bulk MoSe2 Controlling the Gas Flow Kim Jeonghun, Na Liu, Coo Sooho and Sunkook Kim; Sungkyunkwan University, Suwon, Korea (the Republic of).

Two-dimensional transition metal dichalcogenides (TMDs) have attracted researchers for their broad application in semiconductor industry. As their controllable band gap, electronic characteristic and unique optical characteristic are suitable to fabricate electric device such as field-effect transistor. Here we show a synthesis method to control the quality of the bulk MoSe2 using chemical vapor deposition. Argon and hydrogen are the most popular carrier gas and reducing gas, respectively. The ratio of Ar and H2 determines the quality of the MoSe2. Furthermore, the crystallinity increased with increasing gas flow rate. To investigate the quality and uniformity of the bulk MoSe2, Raman spectroscopy, scanning electron microscope, energy dispersive analysis of X-ray, and X-ray photoelectron spectroscopy were performed. MoSe2 thin film transistor was then fabricated with typical bottom gate structure on a SiO2/Si substrate with Al2O3 passivation. The room-temperature carrier mobility for the device was about 21 cm2/Vs. This study demonstrates the novel approach in growth MoSe2 with high crystallinity and its application to electronic devices.

QN03.10.41
Gate-Controlled Photovoltaic Effect of Black Phosphorus/WSe2 Heterojunction Dohyun Kwa, Min-Hye Jeong, Hyun-Soo Ra, A-Young Lee and Jong-Soo Lee; Department of Energy Science and Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, Korea (the Republic of).

Semiconductor two dimensional (2D) materials have shown great potential in optoelectronic devices because of their high carrier mobility and very thin thickness. Recently, many groups have explored the heterojunction structures based on semiconducting 2D materials for photovoltaic applications as ultrathin p-n diodes. For high-performance photovoltaic devices, the electron-hole balance is an important parameter because it has effect on the formation of the built-in field across the device. In this study, we exhibit multi-layer black phosphorus (BP)/WSe2 p-n heterojunction device and demonstrate the photovoltaic effect of the device by electrostatically controlling carrier concentration into BP. The gate-controlled heterojunction device exhibits a high current rectification of 105, external quantum efficiency of 4.4% under the 405-nm laser illumination, and solar efficiency of 4.6% under the AM 1.5 solar spectrum. Our works suggest that making a balance of charge carriers in the 2D heterojunction p-n diode is highly prioritized for the high performance 2D
Atomically thin graphene exhibits fascinating mechanical properties, although its hardness and transverse stiffness are inferior to those of diamond. So far, there has been no practical demonstration of the transformation of multilayer graphene into diamond-like ultrahard structures. Here, we show that during nanoindentation at room temperature, 1-layer graphene on SiC(0001) (1 layer graphene + buffer layer) exhibits a transverse stiffness and hardness comparable to diamond, showing resistance to perforation with a diamond indenter and a reversible drop in electrical conductivity upon indentation. Density functional theory calculations suggest that, upon compression, the 1-layer graphene film transforms into a diamond-like film, producing both elastic deformations and sp$^2$ to sp$^3$ chemical changes. Experiments and calculations show that this reversible phase change is not observed for a single buffer layer on SiC or graphene films thicker than two layers. Indeed, calculations show that whereas in 1-layer graphene layer-stacking configuration controls the conformation of the diamond-like film, in a multilayer film it hinders the phase transformation. Our findings identify supported 1-layer graphene as an interesting candidate for pressure-activated adaptive ultrahard and ultra-thin films and for force-controlled dissipation switches. Our study opens up new ways to investigate graphene-to-diamond phase transitions at room temperature in low-dimensional systems. Finally, this work suggests a new route to produce and pattern single-layer diamond in graphene through stabilization of the diamond-like phase, with applications ranging from nanoelectronics to spintronics.

8:15 AM QN03.11.02
High-Bias Characterization of Single-Crystalline $\text{WTe}_2$ Nanobelts for Future Nanoscale Interconnects

Hwa Kim$^1$, Jong Hwa Kim$^1$, Jae-Ung Lee$^2$, Jong Uk Kim$^3$, Hyung Duk Yun$^4$, Yeeseon Sim$^5$, Jaewon Wang$^5$, Do Hee Lee$^6$, Shi-Hyun Seok$^7$, Ta Il Kim$^8$, Hyongsik Cheong$^9$, Zonghoo Lee$^{10}$ and Soon-Yong Kwon$^{11}$

As elements of electronics are downsized to the nanoscale, the microstructure is no longer stable under current stress in practical applications. For example, conventional interconnect metals (i.e., poly-crystalline Cu and W) suffer from size effects related to both surface and grain boundary scatterings, thus impeding current injection into the materials contributed by the exponentially increased resistivity.$^{(1)}$ Accordingly, high current-carrying van der Waals (vdW) metals such as quasi-one-dimensional (quasi-1D) transition metal (TM) chalcogenides (i.e., TiS$_2$, TaSe$_2$, and WTe$_2$)$^{(2-5)}$ have drawn new attention as alternatives for downscaled interconnects owing to their dangling-bond-free surface and quasi-1D atomic intermetallic bonds, which allow highly mobile carriers to reduce their diffusive motion. However, a lack of reliable bottom-up approaches to obtain high-quality 1D single crystals on a desired substrate hinders systematic electrical characterizations and further applications of the materials. Moreover, a high-bias analysis of TM chalcogenides depending on size under different ambient environments remains to be studied, which will allow us to understand their electrical breakdown mechanism and energy transfer through different interface dimensions.

In this study, we report an investigation of the low- and high-field electrical properties of single-crystalline $\text{WTe}_2$ nanobelts, mainly focusing on their electrical failure and current-carrying capacity. To synthesize stoichiometric, quasi-1D $\text{WTe}_2$ crystals, a eutectic alloy (e.g., Cu$_2$Te, or Au$_2$Te)$_3$ was introduced to provide a liquid-like Te-rich ambient condition. Because of this approach, a systematic investigation of the electrical properties of the crystals became possible as a function of channel dimensions by avoiding degraded edges by harsh etching$^{(6)}$ and random crystalline orientations,$^{(7)}$ which are unavoidable for the exfoliated flakes. The resultant $\text{WTe}_2$ nanobelts could sustain significantly high breakdown current densities ($J_D$) of up to ~100 MA/cm$^2$ and electrical input power per channel length of ~16.4 W/cm, which are higher than those of conventional interconnect metals and any other TM chalcogenides to date.$^{(8)}$ The energy dissipation and carrier scattering models exploited in this study revealed that the high current-carrying capacity of the quasi-1D products is because of a rather scattering-free transport behavior as well as suppressed electromigration in the encapsulated devices until the channels’ breakdown, as compared to the air-exposed ones. We believe that our strategy sufficiently promises the potential for applications in future downscaled nanoelectronics owing to the unique fundamental electrical characteristics of the quasi-1D layered $\text{WTe}_2$ single crystals compared to other vdW materials.

The low density of 3D structures can allow efficient charge carrier transport in the films and the low film resistivity ensured by these novel processes showcase a strong potential for implementation in electronic devices.


8:45 AM QN03.11.04
Layered Perovskite Nanofiber Heterojunctions with Tailored Diameter to Enhance Photocatalytic Water Splitting Performance André Bloesser and Roland Marschall.
University of Bayreuth, Bayreuth, Germany.

Controlled heterojunction design was combined with diameter-tailored electrospinning to prepare mesostructured photocatalysts, leading to strongly enhanced photocatalytic water splitting rates. The (111)-layered perovskite Ba$_3$Ta$_2$O$_7$ [1] in heterojunction with Ba$_3$Ta$_3$O$_{10.5}$ [2] was for the first time prepared as nanofibers by means of electrospinning, including variation of the fiber diameter. [3] The result is a tailored mesostructured heterojunction leading to hydrogen evolution reaction rates from water/methanol mixtures of up to 4.4 mmol h$^{-1}$ with a photocatalyst, and remarkable water splitting activity after Rh−Cr$_2$O$_3$ decoration with hydrogen production rates up to one mmol h$^{-1}$. Our studies also confirm the photocurrent doubling effect of sacrificial alcohols exhibiting α-H atoms with this heterojunction, in contrast to tert-butanol.


9:00 AM QN03.11.05
Designer Synthetic 2D Materials—The Cases of Xenes and Anisotropic MoS$_2$ Alessandro Molle; CNR-BIMM, Agrate Brianza, Italy.

Making adjustable two-dimensional (2D) materials is an emerging route to reach a superior control of functional properties and access new device performances or applications. With this aim in mind, here I will give consideration to two distinct cases. On one hand is the case of the epitaxial Xenes, an emerging class of 2D monoatomic lattice beyond graphene; on the other hand is the anisotropy design in MoS$_2$ nanosheets. By close analogy with graphene, epitaxial Xenes are comprised of monoatomic elements arranged in a honeycomb lattice but unlike graphene, Xenes are epitaxially grown on substrates and exhibit a varying degree of buckling and/or puckering in the lattice structure [1]. Examples in this respect are silicene, germanene, stanene, borophene, epitaxial phosphorene, and recently synthesized antimonene and tellurene. Buckling in Xenes can be taken as a leverage to tune the electronic and quantum properties making it possible for Xenes to appear as semiconductors, semimetals, metals topological and trivial insulators. Not only the wealth of electronic states in the Xenes makes them suitable as nanotechnology platforms, but also topological transitions among these electronic states are predicted to take place as a function of an external solicitation (e.g. vertical electric field, applied stress) thus paving the way to the full exploitation of topology in devices at the 2D level. I will focus on silicene as representative story [2]. Then I will show the route and challenges for Xenes to be integrated in nanoelectronic devices by briefly describing a universal approach to Xene processing and eventually the concept of a topological field effect transistor.

A different case of morphology design at the 2D level is the chemical vapour deposition of MoS$_2$ nanosheets on patterned substrates. The highly conformal character of the MoS$_2$ growth allows for the achievement of an anisotropically modulated MoS$_2$ nanosheet where the phonon and electronic properties are observed to be strongly morphology dependent. The so-induced morphological anisotropy is reflected in the anisotropy of the physical characteristics, such as the phonon spectrum, intrinsic charge fluctuations, and the exciton dynamics. Implications on the band-gap and exciton engineering will be discussed, and the potential for applications envisioned [3].


9:30 AM QN03.11.06
Vapor-Phase Amine Intercalation for the Rational Design of Photonic Nanosheet Sensors Bettina V. Lchtsch 1,2; 1Nanochemistry, Max Planck Institute for Solid State Research, Stuttgart, Germany; 2Chemistry, University of Munich (LMU), Munich, Germany.

The development of vapor sensors with tunable sensitivity and selectivity based on rational molecular design is challenging, however at the same time of great interest due to the manifold applications in our everyday life, e.g. in air quality monitoring or food control. Here, we introduce a design concept for photonic vapor sensors based on stimuli-responsive, swellable 2D nanosheet materials. Antimony and tantalum phosphate (H$_3$Sb$_3$P$_2$O$_{14}$ and HMP$_2$O$_{8}$ (M = Sb, Ta) nanosheet-based Fabry-Pérot interference sensors as manifold applications in our everyday life, e.g. in air quality monitoring or food control. Here, we introduce a design concept for photonic vapor sensors based on stimuli-responsive, swellable 2D nanosheet materials. Antimony and tantalum phosphate (H$_3$Sb$_3$P$_2$O$_{14}$ and HMP$_2$O$_{8}$ (M = Sb, Ta) nanosheet-based Fabry-Pérot interference sensors as touchless displays based on humidity responsive 2D nanosheets.


10:00 AM BREAK
10:30 AM QN03.11.07
Pulsed Laser Deposition Conversion of 2D Transition Metal Dichalcogenides to Form Alloys and Vertical Heterojunctions Yu-Chuan Lin,1 Yiling Yu1 Chenze Liu1,2,3 Alexander A. Puretzky1,3, Mina Yoon1, Christopher M. Rouleau1, Gyula Eres1, Gerd Duscher2,7, Kai Xiao1 and David B. Geohegan1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

The nonequilibrium nature of laser-based synthesis and processing provides a promising alternative for the synthesis of van der Waals alloys and heterostructures of 2D transition metal dichalcogenides (TMD). Using chalcogen vapor plumes generated by pulsed excimer laser ablation of solid S, Se, or Te targets in vacuum and low-pressure background gases, the chalcogen composition of existing 2D crystal monolayers or multilayers can be digitally modulated to form new alloys or vertical heterostructures in order to controllably alter and explore their optoelectronic properties. In this talk, starting with existing monolayer and bilayer WS$_2$ or WSe$_2$ grown on various substrates (and suspended) we demonstrate the versatility of this approach to adjust the composition and property-tune mixed WS$_2$WSe$_2$, monolayers, and partially convert bilayers to form vertical heterojunctions. In both cases, depending on the global strain inherent in the initial TMD crystal (resulting from the initial growth at elevated temperatures), the plasma-induced
exchange of S-Se atoms in the TMD layer creates an additional biaxial strain that can subsequently induce unfavorable cracks or wrinkles in the 2D alloys. However, by choosing a suitable thermal expansion coefficient for the substrate for the initial growth of the 2D crystals, we show that the additional biaxial strain-induced deformation induced by chalcogen replacement can be mediated to allow the 2D crystals to avoid wrinkles and cracks, while retaining their lattice structure. Using this pulsed laser deposition conversion approach, we demonstrate that a homogenous bilayer TMD (e.g., a WS₂ bilayer) grown by chemical vapor deposition (CVD) can be converted into vertical heterojunctions, such as bilayer WS₂–WS₂. The conversion of different bilayer stacking configurations is explored. Photoluminescence and Raman spectroscopy, and scanning transmission electron microscopy confirm that the original bottom layer is nearly intact, even when the top layer is fully converted into another chalcogen composition. Second harmonic generation measurements reveal that the degree of conversion of the top layer depends on the crystallographic stacking between the top and bottom layers. For example, while the 2H-stacking configuration of bilayer WS₂ is found to be the most stable under Se plume irradiation, other stacking configurations are found to have lower thresholds for chalcogen replacement, enabling full conversion of the top WS₂ layer to WSe₂ at 350 °C to form a vertical heterostructure. This approach provides a simple and efficient way to fabricate both 2D alloys and vertical heterostructures.

10:45 AM *QN03.11.08
Enabling Flexible 2D Materials Through Laser Transformation Nicholas Glavin; Air Force Research Laboratory, Dayton, Ohio, United States.

Two-dimensional (2D) materials have the potential to enable flexible electronic devices with exceptional properties for future wearable sensors. One major hurdle still to overcome is the limited growth and processing schemes to manipulate these unique materials on flexible substrates. In this talk, we will discuss using lasers and other light sources to locally transform 2D MoS₂, WSe₂ and heterostructures on polymeric substrates for controlled crystal structure, chemistry and functionalization at both a local (<10 μm) and global (>1cm²) scale. To understand the transformation process, kinetics studies using in-situ spectroscopy enabled insight into fundamental crystal formation and conversion of amorphous to crystalline MoS₂. This information enabled direct laser writing of 2D materials on flexible substrates for controlled crystal structure for sensing applications. Additionally, circuits were constructed out of the laser transformation of 2D materials to form various crystal structures and oxide phases with altering electronic properties. Finally, large area, wafer-scale crystallization of stretchable 2D photodetectors with the use of a broadband pulsed lamp source demonstrate the feasibility of large scale transformation as a means to create unique device constructs. The versatile technique of laser manipulation of 2D materials directly on polymer substrates can potentially enable truly revolutionary flexible electronics based on the unique van der Waals structures.

11:15 AM QN03.11.09
Band Gap and Interface Engineering of Atomic Layered Semiconductors Weihao Zheng, Honglai Li, Tiefeng Yang, Biyuan Zheng and Anlian Pan; Hunan University, Changsha, China.

Two-dimensional (2D) layered semiconductors, notably transitional metal dichalcogenides (TMDs), have recently attracted considerable interest, due to their atomically thin geometry, unique electronic and optical properties and potential applications in integrated nanosystems. Band gap and interface engineering within these nanostructures is fundamentally important to design and create semiconductor heterostructures with tailored electronic band structures for diverse functions and applications[1-7]. Although significant effort and progress have been made to realize composition modulation among different chalcogenide nanostructures, precisely spatial band gap modulation within single 2D semiconductor nanostructures has always been a considerable challenge. In this talk, I will report our recent progress on the band gap and interface engineering of 2D atomically thin layered materials. I will show how to realize composition and band gap continuously modulated 2D semiconductors through alloying of two semiconductor compounds with different band gaps[8-9], and how to achieve sharp interfacial composition profiles of 2D semiconductor heterostructures through the real-time composition control[10]. More importantly, the growth control of 2D atomic layered heterostructures: lateral epitaxy vs. vertical stack[11], and some interesting optical and optoelectronic properties and device applications of these novel nanostructures will also be exhibited. In addition, I will reveal the strain-tuning atomic substitution mechanism of 2D semiconductor materials, which is driven by the strain between the substituted and host lattices[8, 10].

References:

SESSION QN03.12/QN01.11/QN02.10: Keynote: Joint Session: Materials Science with Two-Dimensional Atomic Layers
Session Chair: Deep Jariwala
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 129 A

11:30 AM *QN03.12.01/QN01.11.01/QN02.10.01
Materials Science with Two-Dimensional Atomic Layers Pulickel Ajayan; Department of Materials Science and NanoEngineering, Rice University, Houston, Texas, United States.

There has been tremendous interest in recent years to study two-dimensional (2D) atomic layers which form building blocks of many bulk layered materials. This was started by the spectacular discovery of graphene. This talk will focus on the materials science of the emerging field of 2D atomic layers of various compositions. Several aspects that include synthesis, characterization of defects, doping and manipulation will be explored with the objective of achieving functional structures with atomic layer building blocks. The concept of nanoscale engineering and the goal of creating new artificially stacked van der Waals solids and 3D constructs will be discussed through a number of examples including graphene and other 2D layer compositions. The talk will explore the emerging landscape of 2D materials systems that include hybrid compositions and multi-component 2D alloys. Some of the anticipated applications of these materials will also be discussed.

SESSION QN03.13: Photonic Properties and Devices II
Session Chair: Victor Brar
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 129 A

1:30 PM *QN03.13.01
This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, boron nitride (h-BN), and transition metal dichalcogenides (TMDs). The results span from fundamental measurements and simulations, to devices, to system-oriented applications which take advantage of unusual 2D material properties. On the fundamental side, we have measured record velocity saturation in graphene [1,2], as well as the thermal properties of graphene nanoribbons [3]. These are important for electronic applications, which can exhibit substantial self-heating during operation [4]. Taking advantage of low cross-plane thermal conductance, we found unexpected applications of graphene as ultra-thin electrode to reduce power consumption in phase-change memory [5]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

We have grown monolayer 2D semiconductors by chemical vapor deposition over cm² scales, including MoS₂, with low device variability [7], WSe₂, MoSe₂ – and multi-layer TMDs MoTe₂ and WTe₂ [8]. Importantly, ZrSe₂ and HfSe₂ have native high-K dielectrics ZrO₂ and HfO₂, which are of key technological relevance [9]. Improving the electrical contact resistance [10], we demonstrated 10 nm transistors using monolayer MoS₂, with the highest current reported to date (∼400 nA/µm), approaching ballistic limits [11]. We also directly measured the saturation velocity and saturation current in monolayer MoS₂, finding it is thermally-limited (i.e. by device self-heating and phonon scattering) to about one-third of that of silicon and about one-tenth of that of graphene [12]. Using Raman thermometry, we uncovered low thermal boundary conductance (∼15 MW/m²K) between MoS₂ and SiO₂, which could limit heat dissipation in 2D electronics [13]. We are presently exploring unconventional applications including thermal transistors [14], which could enable nanoscale control of heat in “thermal circuits” analogous with electrical circuits. These studies reveal fundamental limits and new applications of 2D materials, taking advantage of their unique properties.


2:00 PM *QN03.13.02
Emerging Device Applications of 2D Materials
Luke Sweetlock, Vincent Gambin, Philip Hon and Jesse Tice; NG Next, Northrop Grumman Aerospace Systems, Redondo Beach, California, United States.

Two-dimensional materials exhibit unique and dramatically tunable optical and electronic properties. In this seminar, we will describe the fundamental exploration of some of these extraordinary properties, and how these materials are leveraged to create improved or even fundamentally novel devices that point towards impactful applications. A common theme throughout will be the value of highly interdisciplinary and collaborative discovery.

Highly voltage-tunable optical properties will be described in the context of graphene/gold heterostructure metasurfaces. Smooth modulation is observed in the reflected phase of infrared light of over 200 degrees at an infrared wavelength of 8.7 microns [1]. This fast optoelectronic tuning mechanism could enable photonic phased arrays for beamsteering and other high speed reconfigurable elements.

Thinatomically materials can also exhibit novel functionality which is without direct analog in bulk media. For example, an active material developed by oxidation of 2D boron nitride demonstrates formation of atomic scale conductive filaments under electronic bias, exhibiting memristive switching with femtojoule energy consumption [2].

Many emerging device concepts exploit the strong anisotropy of 2D materials and their properties. Multilayers comprised of 2D semiconducting MoS₂ exhibit strong anisotropy between lateral within-layer conduction and interlayer vertical transport, as well as inhomogeneous vertical carrier distribution. From systematic study of charge transport in these structures, a new mechanism for negative transconductance (NTC) device implementation is observed [3].

We have also demonstrated wafer-scale graphene systems for analog dot product computation [6].

References:

2:30 PM BREAK

3:00 PM *QN03.13.03
Colloidal β-In₃Se₃: Monolayer Nanosheets and Their High Photoresponsivity
Sandeep Ghosh; The University of Texas at Austin, Austin, Texas, United States.

The advent of graphene in the recent years has led to widespread investigations on two-dimensional (2D) semiconductors of layered metal chalcogenides (LMCs). This is mostly directed towards their ultrathin and flexible electronic applications as many 2D LMCs interact strongly with light, exhibiting high-power-density optoelectronic devices. This is especially true for those 2D LMCs which comprise of post-transition metals (like In₃Se₃ here), when compared to their transition metal counterparts. Although vacuum deposition and micromechanical cleavage are the most popular techniques for producing high quality 2D LMCs, they suffer from limitations like costly high temperature instrumentation and polydispersity sampling (respectively). Colloidal chemistry, in this regard, offers an alternative low temperature synthetic route with unique morphological control. In this presentation, we will describe the colloidal synthesis of single-layer β-In₃Se₃ nanosheets with lateral sizes tunable from ~300 to ~900 nm. Such synthesis of a single layer of this material, which is five-atom thick (Se-In-Se-In-Se), was accomplished by using short aminonitriles (decyandiamide or cydanamide) as shape controlling agents in a two-stage hot injection process. Discerning the phase of our synthesized nanosheets was particularly challenging since the In₃Se₃ system exhibits intricate polymorphism, especially in the few layer range. A combined analysis comprising of HRTEM and XRD with ED was employed for this. The intensity ratio between two diffraction peaks from two-dimensional slabs of the various phases were compared, which were determined by diffraction simulations in the first place. This was further corroborated by comparing and fitting the experimental X-ray diffraction pattern with Debye formula simulated patterns and also with side-view HRTEM imaging and simulation. The as-synthesized β-In₃Se₃ nanosheets were found to be indirect band gap semiconductors (Eg = 1.55 eV). Single nanosheets were then contacted by Ti/AI or Ti/Au electrodes in order to fabricate photodetectors which showed high photoresponsivities (of the order of 10⁷ A/W at few pW laser power) at low laser power and fast response times (order of few milliseconds). These values of photoresponsivity and response times are comparable to the best photodetectors based on single- and few-layer 2D semiconductors that were reported so far, and in particular to those of multilayer β-In₃Se₃, which implies a higher photoresponsivity per layer in the monolayer regime.

3:15 PM *QN03.13.04
Advanced Optoelectronics Based on Active Metasurfaces
Yu Yao, Ali Basiri, Jing Bai, Xiaohui Chen, Chao Wang and Zubair Rafique; School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona, United States.

Optical metasurface refers to a kind of nanostructured material with sub-wavelength thickness and on-demand optical properties. By rationally engineering the metasurface structures, one could achieve new capabilities for the manipulation of light, e.g., ultra-thin flat lenses, waveplates and holographic plates. In this talk, I will present the unique capability of metasurfaces to address the fundamental limitations in traditional optical materials and realize ultra-compact optoelectronic devices with various functionalities, which are highly desirable for practical applications.

I will discuss about recent progress on mid-infrared modulation based on metasurface integrated with active tuning element. I will first discuss novel design concepts and device implementation of modulators with large modulation depth and broad bandwidth, followed by a summary of our recent progress on system implementation of spatial light modulation and wavefront control. I will also present how to exploit the great flexibility of metasurfaces to manipulate light and enhance light matter interaction in nanometer-size structures to enhance the performance and enable unique functionalities of photodetectors. I will discuss about various schemes we have implemented to enhance infrared photodetection in graphene-metasurface hybrid structures. Moreover, I will also briefly discuss about a full-stokes polarimetric imager sensor with chip-integrated metasurfaces.

3:45 PM *QN03.13.05
Heterogeneous Exciton Engineering of Two-Dimensional Materials on 3D Wrinkle Architectures
Jin Myung Kim¹, Jaepil So², Michael Cai Wang³,⁴, Hong-Gyu Park⁷ and
Strain engineering has been a promising approach to control exciton dynamics and photoluminescence properties of two-dimensional (2D) semiconductors. In particular, strain concentrated on submicron area of 2D WSe$_2$ or WS$_2$ is known to create quantum emitters by exciton funneling and exciton confinement through bandgap gradient. While the previous approaches have introduced 2D layers suspended on top of nano- or micro-patterns to achieve spatially deterministic strain, predictability and modulability of strain have been limited due to challenges in interface control (e.g., uniformity) and dynamic configurability (e.g., rigid substrate). Here, we present predictable and reconfigurable strain gradient in atomically-thin WSe$_2$ via three-dimensional (3D) elastomeric wrinkle architectures. This approach allows 2D WSe$_2$ to be deformed conformally along the wrinkled substrate comprised of a stiff skin layer (SiO$_2$) on top of a soft polydimethylsiloxane (PDMS) substrate. As a result, the strain exerted on WSe$_2$ was periodically changed to tensile and compressive strains at peaks and valleys of the wrinkles, respectively. By tuning wrinkling parameters (e.g., prestrain, skin layer thickness) and encapsulation methods, we were able to achieve photoluminescence (PL) emission shift of as much as 123 meV, corresponding to approximately 2.3% strain. Furthermore, thanks to the use of elastomeric substrate, the applied strain can be tuned reconfigurably by post stretching/releasing processes, with PL shift dynamically modulated. Time-resolved PL decay measurements revealed heterogeneous exciton recombination where tensile strain leads to longer exciton lifetime compared to unstrained or compressive strained regions. Our results demonstrate a 3D architecture based active platform not only for excitation engineering of 2D semiconductors, but also for other strain-responsive 2D devices which can exploit the merits of spatially and dynamically controllable strain engineering.

4:45 PM QN03.20.07
Mechanically Crumpled All-2D Material Photosensor for Enhanced Photosensitivity Juyeong Lee, Pilgyu Kang, Jihan Mun, Yeageun Lee, Sang-Woo Kang and Sung-Woo Nam
University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; Korea Research Institute of Standards and Science (KRISS), Daejeon, Korea (the Republic of)

Atomically-thin two-dimensional (2D) materials provide a unique and promising platform for optoelectronic applications due to their optical, electronic, and mechanical properties. Monolayer molybdenum disulfide (MoS$_2$) is one of the most widely studied semiconducting 2D materials for photosensors with its direct bandgap. Despite of advantageous features of 2D materials, the low optical absorption of monolayer MoS$_2$, resulting from its single-atom-thickness, limits higher photosensitivity. In this presentation, we report a mechanically self-assembled, crumpled MoS$_2$ photosensor with graphene electrodes. We use graphene as electrodes in our all-2D photosensor because of its mechanical robustness, electrical conductivity and barrier-free contact to MoS$_2$. Our photosensor exhibits (i) enhanced photosensitivity from crumpled MoS$_2$ structure, (ii) high stretchability with mechanical durability, and (iii) anisotropic photocurrent generation from anisotropic topography via exciton funneling effect. We demonstrate enhanced internal photosresponsivity of our crumpled MoS$_2$ photosensor, by comparing with flat MoS$_2$ photosensor. Our photosensor was further stretched up to 150% without introducing major structural damage, and mechanical durability of the sensor was verified with 1000 cycles of stretching-releasing test. Our approach to mechanical self-assembly of atomically-thin materials offers a simple but effective way to enhance photosensitivity and suggests a new way to engineer exciton funneling in 2D material system.
We investigated the fundamental origin of material degradation and developed a surface-engineering approach to render few-layer black phosphorus stable for several months in ambient conditions. The findings revealed that the key cause of degradation is photo-oxidation which is specifically accelerated when the material is exposed to UV light. Building on this knowledge, we used an ionic liquid on the surface that sequesters reactive oxygen species (ROS) that are responsible for surface deterioration.[3] We further created a dry-etch procedure to control the layer-thickness (hence bandgap) and engineer controlled defects in the material.[4] Subsequently, the defect engineered layers were exploited to generate unique photoresponse in BP which was deployed to mimic neural synaptic interfaces using optical stimuli.

In summary, we have conducted a full suite of studies ranging from understanding the fundamentals of degradation to developing protection techniques without interfering with the desirable properties of 2D BP. Subsequently, we report a simple defect engineering strategy and exploit them for various functionalities including the creation of an artificial optical synapse.


8:15 AM QN03.14.02

Ionic Substrate Effects on Graphene
Karen Long1, Adam Friedman2 and Jeremy Robinson3; 1Naval Surface Warfare Center, Dahlgren, Virginia, United States; 2Laboratory for the Physical Sciences, College Park, Maryland, United States; 3U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

While graphene is well known to have exceptional electrical properties, those properties can be greatly affected by its substrate. Electron-phonon scattering has been shown to contribute to the optical absorption and interaction with polar substrate phonon modes in order to control electron transport. Instead of polar substrates, we have investigated graphene and graphene nanoribbons on BaF2. The BaF2 is grown epitaxially on either Si, resulting in (111) BaF2 or GaAs, resulting in (100) BaF2 which is lattice matched. As a result, unlike SiO2, we have an atomically crystalline surface upon which CVD grown graphene sheets are placed and then formed into nanoribbons by ion lithography. BaF2 has a wide Strahlenband around 50um, making it a good candidate for coupling to surface phonon plasmons in the far IR. To study the substrate effects, we use EFMs AFMs which provides a relationship between the electrostatic potential and the voltage applied to the tip. By mapping the phase change vs voltage, we can obtain the work function. EFS measures the force gradient versus the force providing a better resolution of the electrical properties. Since BaF2 grows (111) on Si by forming triangles in three directions, we can use STM to determine edge effects which can be polar. In building, heterostructured materials it is important to understand the valence band offset and the heterostructure interface. We use XPS spectra of the valence band to obtain the valence band offset formed from a BaF2 surface.

8:30 AM QN03.14.03

Scanning Tunneling Microscopy and Spectroscopy of Wet Chemically Synthesized Porous Graphene Nanoribbons
Kaitlyn Parsons1, Adrian Radoseva2, Mohammd Pour1, Tao Sun1, Narayana Aluru1, Alexander Sinitskii2 and Joseph Lyding1; 1Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States; 2Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States; 3Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 4Mechanical and Science Engineering, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois, United States.

The bottom-up wet chemical synthesis of graphene nanoribbons (GNRs) opens interesting opportunities for tailoring the GNR structure with atomic precision [1]. Atomically precise porous GNRs are a new chemically synthesized variation for which the fabrication procedure yielding multiple pores in a single ribbon and the electronic details of the ribbon have not been reported. In this work, porous GNRs are dry contact transferred in ultrahigh vacuum to clean silicon and III-V semiconducting substrates and examined using UHV scanning tunneling microscopy (STM) and spectroscopy (STS). STM imaging confirms the expected porous structure and indicates a unique electronic feature at the graphene nanopores, and STS measurements indicate a 2.0 eV bandgap. These results are compared to first-principles DFT simulations in which an increased local density of states is also reported. Since BaF2 crystals of various thicknesses shows results consistent with our transport measurements. A GW correction predicts a 3.24 eV bandgap. Illumination of pore effects in GNRs contributes to an increased understanding of the tunability of GNR electronic structure. Porous GNRs have potential applications in molecular filtration, detection and DNA sequencing.

References


9:00 AM QN03.14.05

Graphene-Based Photonic Devices for Terahertz Applications
Peter Qiang Liu; State University of New York at Buffalo, Buffalo, New York, United States.

In recent years, graphene has attracted significant amount of research efforts on multiple fronts in the photonics field, mainly thanks to its attractive material properties such as high carrier mobility at room temperature and large tunability of carrier concentration via electrostatic gating. Development of reliable and high-throughput processes of graphene transfer also make integrating graphene with a wide variety of other materials, structures and devices relatively straightforward. Moreover, in the mid-infrared to terahertz (THz) spectral range, graphene can support highly confined surface plasmon modes with relatively long lifetime, and therefore drastically enhance the light-matter interactions in various processes which can be exploited by a wide range of applications. There has been a plethora of proof-of-concept demonstrations and further developments of graphene-based photonic devices for different applications and spectral regions, and research in these fields is growing rapidly. In this talk, I will present some of our recent work on employing graphene as a key functional material in various photonic devices operating in the THz spectral region, including high-speed modulators, beam steerers, photodetectors and molecular sensors. These devices may facilitate the ongoing development of THz technologies and applications such as THz wireless communications, imaging and sensing.

9:30 AM QN03.14.06

Quantum Transport in Few-Layer Graphene and Phosphorene Devices
Jeannic Lau; The Ohio State University, Columbus, Ohio, United States.

Low dimensional materials constitute an exciting and unusually tunable platform for investigation of integer and fractional quantum Hall states. Here I will present our results on transport measurements of high quality graphene and phosphorene devices. In rhombohedral-stacked tetraylayer graphene, we have observed a large intrinsic gap at half filling, up to
80 meV, that arises from electronic interactions[1]. In Bernal-stacked-tetralayer, we have observed multiple Lifshitz transitions as charge density, magnetic field and displacement field are tuned[2]. In few-layer black phosphorus devices with mobility up to 50,000 cm²/Vs, integer QH states are resolved at a few Tesla, and fractional states at filling factor - 4/3 and -0.56±0.1 are observed[3]. These results underscore the strong electron correlation in atomically thin systems.

The properties of 2D materials can be modified by structural defects, so controlling the nature and concentration of such defects provides a means of tailoring material properties for specific applications [1]. This study examines the effect of ion-irradiation on damage production in graphene, with particular emphasis on the effect of ion fluence and nuclear stopping power (S_n) on the concentration and structure of defects; the significance of collective effects associated with molecular ion irradiation; and the role of the substrate in damage production.

Experiments are conducted on supported (G/SiO₂) and suspended (Gs) graphene films, with the former produced by exfoliation of highly oriented pyrolytic graphite (HOPG) and the latter by chemical vapor deposition (CVD). The films are irradiated with 30 keV H⁺, Li⁺, C⁺, Sr⁺ and Ge⁺ ions to fluences (Ω) in the range 10^{10}-10^{16} ions/cm² and analysed using Raman Spectroscopy (RS). The density and structure of defects are determined from Raman analysis using the phenomenological models of Lucchese et al. [2] and Eckmann et. al. [3], respectively. Substrate effects are assessed by comparing damage in G/SiO₂ and Gs irradiated under identical conditions and by comparing damage in G/SiO₂ irradiated with 30keV C⁺ at incident angles of 30°, 45° and 60° relative to the surface normal. G samples are also irradiated with 60 keV C⁺ ions to assess collective effects resulting from multi-ion interactions.

It is shown that defect production scales with the nuclear stopping power of the ions, and that the structure of the defects evolves with increasing ion-fluence from an initial mix of Stone-Wales defects and divacancies, to defects with an increasing fraction of higher-order topological defects. A comparison of the defects created in suspended graphene films by 30 keV C⁺ ions and 60 keV C⁺ ions further showed that the damage created by dimer ions closely matched that produced by monomer ions with twice the fluence, suggesting that there are no significant collective effects associated with the molecular ion irradiation.

The predictions of reference [4] that ion-irradiation damage in supported graphene films is dominated by recoiling ions and sputtered atoms from the substrate is also tested by comparing defect accumulation in supported and suspended films irradiated under identical with 30 keV C⁺ ions. No significant difference in defect density is observed for the two samples, clearly showing that defect production is dominated by direct collisions with C atoms in the graphene layer, a conclusion that is further supported by data from variable incident angle studies.

References


10:45 AM QN03.14.08
Interfacial Slip and Deformation in 2D Electromechanical Systems Arend M. van der Zande; Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Due to their unparalleled mechanical strength, and stability down to a monolayer, atomically-thin membranes made from two dimensional (2D) materials like graphene and MoS₂ represent the ultimate limit in size of mechanical atomic membranes. Yet, many of the most interesting properties of 2D materials and new functionality arise from the interfaces between layers and in engineering multilayer heterostructures. The last few years have led to a revolution in nanoelectronics from 2D heterostructures where layer-by-layer stacking of monolayer 2D materials with disparate electronic properties leads to functional nanometer scale electronic devices. An open question is how to integrate the outstanding mechanical properties of 2D materials with the enhanced functionality of heterostructures to enable new technologies like 3D foldable circuitry, nanoscale origami, or resonant NEMS utilizing 2D heterostructures as active electronic and mechanical components. In this presentation, we will examine the mechanics of deformation of 2D atomic membranes, the emergence of interlayer slip in van der Waals interfaces, and their impact on nanoelectromechanical systems.

We measure the morphology of multilayer graphene transferred onto steps in a hBN substrate. We find the graphene conforms with nanoscale curvatures down to 1 nm, which is allowed by the introduction of slip dislocations between the graphene layers. From the curvature, we find that the bending modulus of the slipped graphene is linearly dependent on the number of layers rather than the cubic dependence that would be predicted from continuum mechanics. Next, we examine the evolution of buckle and fold instabilities in uniaxially compressed graphene and MoS₂ by measuring the topography under increased compression. We observe a material dependent transition from delamination and new fold generation to slip and growth of existing folds. Through a simple energy conservation model, we predict this transition and use it to extract the material dependent interfacial friction. Finally, we engineer electromechanical resonators from atomically thin bimorphs of graphene/MoS₂ as well as twisted bilayer graphene. We observe new features in the tuning behavior of the resonators, including kinks and discrete jumps. These features are not predicted by the tensioned membrane model used to describe the behavior of monolayer 2D resonators, and we attribute them to atomic scale stick-slip behavior in the resonators. Taken together, these experiments show that interfacial slip strongly impacts the mechanics of 2D materials and heterostructures and leads to membranes which are orders of magnitude more deformable than conventional 3D materials. As a result, slip is a critical phenomena which must be considered when engineering mechanically active devices from 2D materials and heterostructures.
Electronic Enhancement of Layered Transition Metal Dichalcogenides via One-Step Chemical Functionalization

Jun Hong Park1, Amritesh Rai2, Jeongwoon Hwang1, Chexi Zhang3, Kyeonggae Cho2, Sanjay Banerjee2 and Andrew Kummel3;* Gyeongsang National University, Jinju, Korea (the Republic of); 2The University of Texas at Austin, Austin, Texas, United States; 3The University of Texas at Dallas, Texas, United States; 4University of California, San Diego, San Diego, California, United States.

In the present report, chemical functionalization is demonstrated to enhance the electrical performance of two-dimensional (2D) layered transition metal dichalcogenides (TMDCs) field-effect transistors (FETs) by applying a one-step dipping process utilizing ammonium sulfide [(NH4)2S] solution. The adsorption process at the surface of WSe2 via chemical treatment is elucidated at the molecular level using scanning tunneling microscopy (STM) and spectroscopy (STS). Molecule resolved STM and STS reveal that the molecular adsorption on monolayer (ML) WSe2 surface induces a band structure transition with the reduction of electronic band gap from 2.1 eV to 1.1 eV and the Fermi level shift towards its valence band edge (VBE), consistent with an increase in the density of positive charge carriers. The electronic transformation of WSe2 with this one-step chemical treatment is confirmed by density functional theory (DFT) calculations which reveal that molecular ‘SH’ adsorption on monolayer WSe2 significantly reduces the energy gap between the valence and conduction bands, consistent with a high density of positive charge carriers. These results suggest that one-step chemical functionalization of 2D layered transition metal dichalcogenides (TMDCs) enables the introduction of rigid functional groups at the surface to induce tailorable electronic properties, opening up opportunities for the development of novel electronic and optoelectronic devices.

SESSION QN03.15: Mechanical Properties and Opto-Electromechanical Effects
Session Chairs: Deep Jariwala and SungWoong Nam
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 129 A

11:30 AM QN03.14.10
Hierarchical Phonons in a Two-Dimensional Superatomic Semiconductor
Kihong Lee1, Xinjue Zhong1, Bonnie Choi1, Daniele Meggioraro1,2, Filippo De Angelis1,2, Xavier Roy1 and Xiaoyang Zhu1;1 Columbia University, New York, New York, United States; 2Istituto Italiano di Tecnologia, Genova, Italy; 3CNR-ISTM, Perugia, Italy.

Designing materials with structural hierarchy is of fundamental interest in materials science since it uncovers unique physical properties and functions. The field of two-dimensional (2D) materials is highly active and rapidly expanding, but hierarchical material design in 2D materials has been challenging. Here, we report a novel 2D semiconductor with a hierarchical structure composed of covalently linked ReSe2 clusters. The material, a 2D structural analogue of the Chevrel phase, is prepared by mechanical exfoliation of the van der Waals solid ReSe2Cl6. Using scanning tunneling spectroscopy, photoluminescence and ultraviolet photoelectron spectroscopy, and first-principles calculations, we determine the electronic band gap (1.58 eV), optical band gap (1.48 eV), and exciton binding energy (100 meV) of the material. The latter is consistent with the partially 2D nature of the exciton. ReSe2Cl6 is the first member of a new family of 2D semiconductors whose structure is built from superatomic building blocks instead of simply atoms; such structures will expand the conceptual design space for 2D materials research.

To demonstrate its unique properties, we bring our attention to hierarchical phonons of the material. Phonon couplings to electrons, excitons and other phonons play key roles in material properties, such as charge transport, thermal transport, light emission, energy transfer, and superconductivity. In conventional atomic solids, such as Si or GaAs, there are only extended phonons as determined by bonding and crystalline symmetry. Phonons are uniquely important in nanomaterials due to quantum confinement and spatial localization in zero, one, and two dimensions (0D, 1D, 2D). In quantum dots, the 0D confinement and local symmetry/interfaces can lead to strong electron-phonon coupling. In 1D carbon nanotubes and 2D graphene or transition metal dichalcogenides, the reduced dimensions also enhance phonon coupling to electrons or excitons. In these materials, their phonon modes are intimately related to their dimensionalities, as demonstrated from radial breathing modes, interlayer sliding modes, and interlayer breathing modes. Here we expand the phonon space by adding localized 0D phonon modes to delocalized phonon modes in a hierarchical superatomic semiconductor. With coherent phonon spectroscopy, we observe three distinct phonons showing strong electron-phonon coupling and correlated with three different steps of dimensional hierarchy. Additionally, these phonons, including the localized 0D breathing of each superatom, the delocalized twisting of superatoms in each 2D layer, and interlayer breathing modes, can be concurrently generated by above-gap impulsive excitation. The presence of local phonon modes in an extended crystal opens the door to controlling material properties from hierarchical phonon engineering.

11:45 AM QN03.14.11
Capillary Origami with Atomically Thin Sheets
Challhlee Choi1, Joeson Wong2, Souvik Biswas2, SungWoong Nam1 and Harry Atwater3;1 Mechanical and Science Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States.

Origami is perhaps best known as an art form that transforms flat sheets of paper into intricate three-dimensional (3D) structures. Inspired by this technique, recent works have demonstrated the folding of two-dimensional (2D) materials into micron-scale structures actuated by thermal and chemical perturbations. "Capillary origami," in which the surface tension of a liquid droplet on a flat sheet causes the sheet to fold, is a particularly attractive origami technique because it can be designed for liquid-liquid interfaces, enabling many biological and chemical applications. Here, we extend capillary origami techniques to 2D materials, using droplets in liquid systems to fold micron-scale polyhedral sheets from monolayer molybdenum disulfide (MoS2), a 2D semiconductor. The geometries of the final folded origami are preprogrammed by lithographic design of different starting shapes and the introduction of rigid metal panels to define hinges. These origami structures are further made self-folding by manipulating the miscibility of the droplets on the sheets, growing and shrinking the droplets to dynamically control folding. This work demonstrates a new avenue for actuating 2D materials into pre-designed 3D structures.
First-principles calculations predict that epitaxial growth of Au on 2D transition metal dichalcogenides (TMDCs) should induce selective strain in the top layer of a multilayer stack. The ability to manipulate strain in this way would have implications for the nanomanufacturing of these materials for opto-electronic devices, such as the ability to modulate the band gap within a single monolayer.

4D scanning transmission electron microscopy (4D STEM) is used to investigate the strain states present in the Au-MoS$_2$ system. Where Au is evaporated onto MoS$_2$, we find consistent compressive biaxial strains up to a stunning 9% in MoS$_2$ as well as previously unreported epitaxial relationships, imposing anisotropic strains, between the two species. Further, it appears that the strain is confined to the monolayer in contact with the Au, while other layers in the structure remain unstrained. These findings open up new avenues of inquiry in the investigation of TMDC-metal interactions.

We will present the results of extensive characterization of the various morphologies and strain states found at the Au-MoS$_2$ interface via 4D STEM. This technique involves recording a selected area electron diffraction (SAED) pattern every few nanometers across a two-dimensional sample area, and the resulting data is a 2-D array of 2-D diffraction patterns, comprising a 4-D dataset. Extremely large, information-rich datasets are produced, which requires a large-scale approach to data analysis. In order to meet this need for high-throughput analysis, we develop a novel machine learning approach that identifies, indexes, and characterizes the 10,000s of SAED patterns in these 4D STEM datasets utilizing a neural network (NN). The NN is trained on simulated diffraction patterns to recognize different crystal species and orientations (e.g., MoS$_2$ [001], Au [111], Au [211]). The strain states of the identified crystals are then characterized using conventional analytical methods.

These findings provide empirical motivation for the Au-assisted exfoliation of TMDCs for anticipated applications in nanoelectronics, photonics, and sensing. Moreover, this evidence of ultrahigh strains bears implications for band gap engineering in monolayer TMDCs. This multidisciplinary work directly integrates modern computer science deep learning techniques with microscopy and materials science, bridging a knowledge gap in the field and opening the door to rapid characterization of nanoscale structures.


2.15 PM QN03.15.04 Photodetector in h-BN Encapsulated Bilayer Graphene Field-Effect Transistor Teerayut Uwanno, Teerayut Uwanno, Takashi Taniguchi, Kenji Watanabe and Kosuke Nagashio; 1The University of Tokyo, Tokyo, Japan; 2College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand; 3National Institute for Materials Science, Tsukuba, Japan.

Recent progress on automatic driving technology further requires infrared detectors with faster response and room temperature operation. Although fast response is achieved for quantum type HgCdTe and quantum-dot infrared photodetector (QDIP), the thermal noise inherently prevents the infrared detection by narrow gap semiconductors at room temperature [1]. Here, bilayer graphene (BLG) phototransistor with the electrically tunable band gap is theoretically suggested to have the IR detectivity even at room temperature because the gate action due to the photoexcited carriers amplify the photocurrent and this amplification can overcome the thermal noise [2]. In order to experimentally prove the current amplification by phototransistor action, the understanding of the basic mechanism behind the photoresponse without phototransistor action is critical. In this study, we investigated the photoresponse to the visible light in h-BN encapsulated direct-gap BLG-FETs on SiO$_2$/Si and quartz substrates. For the visible light detection, a Ni top gate electrode with ~20 nm thickness and ~5 μm width was used. In the transport measurement at 10 K for the BLG heterostructure FET on the SiO$_2$ Si substrate, a pronounced photocurrent was observed around the charge neutrality point and the photoresponse at the charge neutrality point increased with increasing the band gap. Moreover, it was found that photoresponse diminished above 100 K. On the other hand, for the device on the quartz substrate, the photoresponse was quite limited even at 10 K. This comparison suggests that the photoresponse in the present device is dominated by bolometric effect, not by photodetection. In previously reported BLG bolometer with SiO$_2$ top gate [3], the responsivity at the displacement field of 0.65 V/mm disappeared at ~40K, while the responsivity of the present device at the same displacement field was retained up to ~80K. This improvement is because the reduction of charged impurities in the heterostructure with h-BN resulted in stronger temperature dependence of channel resistance at the charge neutrality point.

As a summary, the dominant photoresponse without phototransistor action in h-BN encapsulated direct-gap BLG-FETs is bolometric effect and the bolometric response is much improved than that in the BLG encapsulated with oxides. The phototransistor action will become prominent when the top gate length is reduced to the carrier diffusion length in BLG (~250 nm).


2.30 PM QN03.15.05 Fast Graphene Photodetector with Responsivity >10$^4$ A/W Krishna Murali, Nithin Abraham, Sarthak Das, Sangeeth Kallatt, Medha Dandu and Kausik Majumdar; Indian Institute of Science, Bangalore, Bengaluru, India.

Graphene absorbs light of extremely wide wavelength range owing to its gapless bandstructure. This makes graphene a promising material for ultra-broadband photodetection [1]. In addition, due to high mobility, the graphene photodetectors can exhibit high speed operation [2]. However, there are two important roadblocks that prohibit graphene from being a highly sensitive photodetector. First, graphene being extremely thin material, can absorb only ~2.3% of the incident photons in a monolayer. Second, the lifetime of the photo-generated carriers is very short (~ ps). Thus, it is important to separate them in a time scale less than this to obtain a sizable photocurrent. Most of the graphene detectors, for example, metal-graphene junction [2], graphene p-n junction [3] and biased bilayer graphene [4], thus exhibit low responsivity. In this regard graphene detectors based on photogating effect are attractive which exhibit large responsivity [5-7]. However, these structures often rely on light absorption by a different material, like MoS$_2$ [5] and quantum dot [6], thereby the wavelength of operation is limited to the light absorption threshold of the respective absorbing material. These high-gain photogating devices also exhibit slow transient response with remnant photocurrent, and a gate pulse is often required to flush trapped carriers and restore initial state [5, 7] – necessitating additional circuit.

We propose and experimentally demonstrate a new class of photodetector using graphene/WS$_2$/MoS$_2$ van der Waals heterojunction in a floating gate structure. Graphene is used both as light absorbing medium as well as conducting channel in plane. A fraction of the photoelectrons generated in graphene is transferred vertically in an ultra-fast time scale to floating monolayer MoS$_2$ through the WS$_2$ spacer barrier layer. The electrons, after being transferred to MoS$_2$, thermalize in short time scale to the conduction band edge of MoS$_2$. While they can return to graphene by tunneling through WS$_2$ bandgap, a steady state population of electrons is created in a short time scale in MoS$_2$. The transferred photoelectrons in MoS$_2$ in turn electrostatically gate the graphene channel by strong capacitive coupling through the ultra-thin WS$_2$ spacer layer. When light is turned off, the captured electrons in MoS$_2$ swiftly tunnel through WS$_2$ to graphene due to the built-in field, automatically shutting off the gating action. This suppresses remnant photocurrent and no extra gate pulse is required to flush the confined electrons.

The stack is systematically characterized photoluminescence quenching measurement as a function of temperature. The photodetector exhibits a responsivity in excess of 10$^4$ A/W in the NIR regime with a specific detectivity of 1.6x10$^{11}$Jones, which is higher than that of any existing graphene-absorption-based detector by several orders of magnitude. The photodetector also maintains high speed of operation (sub-millisecond transient response) which marks an important step towards building graphene based high speed, ultra-wideband photodetector with high sensitivity across bands.

References:
The tutorial will give an overview of some unresolved theoretical and experimental problems in the field of nanoscale thermal transport. Particular attention will be devoted to the outstanding questions and techniques aimed at understanding non-diffusive transport regimes at the nanoscale where the Fourier law breaks down. The main goal of this tutorial is to present our current understanding of these issues, and give some ideas how to move forward.

In the first part of the tutorial, Prof. Philip B. Allen will discuss when and why the Boltzmann transport theory for phonons fails, and present its possible extensions to the nanoscale. He will also discuss the outstanding issue of defining and measuring the local temperature.

In the second part, Prof. David G. Cahill will provide an overview of what is known and not known in the physics of thermal transport at the nanoscale with an emphasis on experimental studies of materials and their interfaces at temperatures near ambient. In particular, he will discuss the breakdown of the diffusion equation at small spatial and temporal scales.

8:30 AM
Heat Transport – Fundamentals and Theory for Nanoscale  
Philip B. Allen; Stony Brook University, The State University of New York

Crystals have quasiparticle excitations: electrons, holes, phonons, magnons, etc. These particles are “normal modes” of excitation. They have energy Ek, where k “labels” the mode (wave vector k, branch index n, and possibly other indices like spin). They also have velocities, vk=dEk/dk. In equilibrium, the number of particles in mode k is given by the Fermi-Dirac or Bose-Einstein distribution nk. If the system is out of equilibrium, the number of particles in mode k is Nk. These modes all transport heat if the system is out of equilibrium. The heat current is the sum of vkNk. Therefore, the fundamental object of study is the nonequilibrium distribution Nk-nk. The usual method for studying this is the Boltzmann transport equation (BTE). What are the important issues? (1) When and why can the BTE fail? (2) How should the BTE be extended to work for nanoscale heat sources? (3) How is the local temperature defined and measured? None of these questions is fully answered. Partial answers will be discussed. The discussion will focus on heat carried by vibrations in insulators. There are three reasons motivating this choice. (A) Phonons have very diverse mean free paths. Many insulators have lower frequency phonon modes with long mean free paths which can exceed the dimensions of heating elements or measuring probes. These provide interesting challenges to theory and experiment. (B) Phonon quasiparticle modes are easier to deal with in one important sense. At higher temperatures, quantum aspects fade out, and classical ideas, including classical molecular dynamics simulation, become powerful tools. (C) Amorphous and other disordered insulators have vibrational normal modes of diverse character that can be modeled theoretically (for example, in the “propagon/diffuson/locon” picture). Heat conduction in metals is also important, but the dominant electron and hole carriers of heat are less diverse. They are easy to treat in “conventional” crystalline metals, and hard to treat in “exotic” metals.

10:00 AM BREAK

10:30 AM
Current Understanding and Unsolved Problems in Thermal Transport at the Nanoscale  
David G. Cahill; University of Illinois at Urbana-Champaign

On length scales large compared to the mean-free-paths and equilibration lengths of the excitations that carrier heat, the diffusion equation is an accurate description of the relationship between temperature fields and heat fluxes. On small spatial and temporal scales, this simple description fails due to i) scattering and finite transmission of excitations at boundaries; ii) out-of-equilibrium distributions of heat carriers that are induced by heat flow across material interfaces; and iii) non-equilibrium between phonons, electrons, and magnons. In this tutorial lecture, I will provide an overview of what is known and not known in the physics of thermal transport at the nanoscale with an emphasis on experimental studies of materials and their interfaces at temperatures near ambient.

SYMPOSIUM QN04

Nanoscale Heat Transport—Fundamentals  
April 23 - April 26, 2019

Symposium Organizers  
Olivier Delaire, Duke University
Nanoscale Thermal Metrology Using SEM, TEM and Confocal Microscopy

Chris Dames;1,2 University of California, Berkeley, Berkeley, California, United States;2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

I will review several collaborative efforts at developing new non-contact methods for heating and thermometry at the nanometer scale. Examples include techniques based on SEM (e-beam as a point heater; secondary electron yield as a thermometer), TEM (thermometry using the Debye-Waller effect), and confocal microscopy (luminescence thermometry of individual nanoparticles).

A Multi-Temperature Model for Non-Equilibrium Thermal Transport

Xiaolin Ruan, Purdue University, West Lafayette, Indiana, United States.

Conventionally, the two-temperature model has been widely used for electron-phonon coupled non-equilibrium thermal transport. However, many recent applications have shown that different phonon branches can be in strong thermal non-equilibrium. Therefore, assuming a local equilibrium lattice can lead to misleading or wrong results. Here, we present a multi-temperature model to capture the non-equilibrium among different phonon branches, and demonstrate its advantages over the conventional two-temperature model for bulk materials and across interfaces.

Specular Reflection Creates Lowest Thermal Phonon Conductivity

Martin Maldovan; Georgia Institute of Technology, Atlanta, Georgia, United States.

The thermal conductivity of materials is not a fixed physical property but can be manipulated by controlling the transport properties of thermal phonons. Recently, a large number of experiments have been introduced where thermal conduction is reduced by orders of magnitude via phonon mean free path reduction through diffuse surface scattering. In contrast to established work that use the diffuse surface scattering of phonons as the physical mechanism to reduce the thermal conductivities, in this talk we show that the largest reduction of thin film heat conduction is achieved via specular scattering. Our results thus create a new paradigm for heat conduction manipulation since smooth surfaces – in contrast to rough surfaces – can be more effective on suppressing thin film phonon heat conduction.

Phonon Heat Conduction and Nanoscale Disorder—From Scatterings to Localizations

Sebastian Volz; CNRS–University of Tokyo, Tokyo, Japan.

Effect of structural disorder on phonon thermal conduction remains an open question with a large spectrum of physical effects, as the plane-wave description of atomic vibrations is expected to become irrelevant. In a first stage, atomic scale disorder will be investigated in various systems –silicon [1], SiGe nanowires [2], partial-crystal partial-liquid [3], 2D [4,5] - with atomic scale simulations. Secondly, thermal properties of nanoscale random materials [6,7] will be presented to raise the question of the eventual impact of localization on heat conduction.

Far-Field Submicron Thermoreflectance Imaging

Amirkoushyar Ziabari, Sami Alajlouni and Ali Shakouri; Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States.

Self-heating and localized hotspots can limit the performance of electronic and optoelectronic devices. Contact-related artifacts and diffraction limit the accurate temperature measurements at deep submicron scale. Here we combine thermoreflectance (TR) imaging with a robust image reconstruction technique to achieve accurate temperature maps of nanoscale metal interconnects. Reconstructing accurate temperature profiles from far-field diffraction-limited images is an ill-posed inverse problem. To formulate the inverse problem, we developed a model based imaging process technique based on a Bayesian framework that consists of a maximum-a-posteriori (MAP) cost function with Generalized Gaussian Markov random field priors (GGMRF). The imaging system was approximated by a Gaussian blurring kernel using the information about the pixel dimensions, numerical aperture of the lens used in the system as well as the wavelength of the light. The iterative coordinate descent (ICD) optimization is then used to minimize the corresponding cost function and extract the temperature profiles.

We performed the reconstruction both for numerically designed experiments as well as experimental thermoreflectance thermal images. Additionally, statistical analysis of the resolution limit shows that image reconstruction is a strong function of signal-to-noise ratio. We carried out detailed analysis to investigate the impact of the signal-to-noise ratio.
on extracting the accurate temperature of nanoscale features. Theoretical and experimental results demonstrate accurate thermal mapping of objects down to 100nm. The proposed non-contact technique provides an alternative to techniques such as scanning probe that are often slower and quite sensitive to surface roughness. Additionally, the technique can be applied to other far field imaging experiments to study the performance of nanoscale optoelectronic and plasmonic devices.

Since quasi ballistic phonons dominate submicron thermal transport in many semiconductors at room temperature, there are questions about the definition of temperature and what actually a thermometer measures. Transient hyperspectral imaging as well as resistance thermometry are used to study the apparent temperatures of various metals and nearby semiconductors and to verify our submicron TR imaging results. Indications for superdiffusive and hydrodynamic heat flow are briefly described.

2:00 PM QN04.02.02
Pre-Interface Phonon Scattering Effect in Thermal Transport Across Solid Interfaces Eungkyu Lee, Ruiyang Li and Tengfei Luo; University of Notre Dame, Notre Dame, Indiana, United States.

Understanding phonon transport across solid-solid interfaces can greatly impact thermal engineering in many solid-state applications. Conventionally, phonon scattering is considered impediment to thermal transport. In this study, we present systematic study of the effect of pre-interface phonon in thermal boundary conductance using non-equilibrium molecular dynamics (NEMD) simulations. We first examine the fundamental role of anharmonic phonon scattering in thermal transport across an artificial solid junction, which consists of a monatomic lattice and a diatomic lattice. Using interatomic force parameters expanding up to the third-order, we investigate how inelastic phonon scattering processes in the diatomic lattice layer influence thermal boundary conductance. It is found that the anharmonicity inside the diatomic lattice layer promotes phonon-phonon energy conversion between optical and acoustic phonon modes, which eventually lead to enhanced thermal transport across the solid junction by populating more acoustic phonon modes with higher transmission probability through the pre-interface phonon scattering. Importantly, we find that anharmonic scattering effect in the pre-interfacial region is more important than that right at the interfaces in thermal transport. Next, we explore pre-interface phonon scattering effect in thermal transport across SiC/GaN interfaces by doping isotopes in the GaN, where the SiC/GaN interface is of technological importance in power electronics. We use $^{11}$N or $^{35}$Ga as isotopes in NEMD simulations. By tuning various isotope-doping characteristics (i.e., the isotope concentration, skin depth of the isotope region, and its distance from the interface), we investigate an enhancement of thermal conductance across SiC/GaN interfaces. We find that 10% of $^{11}$N isotope in GaN layer can increase TBC by as much as 23% compared to the isotopically pure cases. In addition, when the isotope-doped region is located away from the SiC/GaN interface, the TBC enhancement still exist, showing pre-interface phonon scattering by isotopes is mainly responsible for the enhanced TBC. Moreover, analysis of spectral temperatures of phonon modes reveal that heat transfer rates by low frequency phonons ($< 20$ THz) across SiC/GaN interfaces increase after isotopes are introduced.

Our studies demonstrate that pre-interface phonon scatterings can help redistribute phonon energy, so that phonon modes with higher transmission probability can be more populated, which leads to TBC enhancements across solid-solid interfaces. Development of new theoretical models should consider this pre-interface phonon scattering effect. Practical materials design can also take advantage of this effect to enhance interfacial thermal transport.

2:15 PM QN04.02.03
Predicting the Phonon Mode-Resolved Specularity Parameter Using the Atomistic S-Matrix Method Zhuo-Yong Ong; Institute of High Performance Computing, Singapore, Singapore.

The phonon specularity parameter represents the probability of the phonon being specularly scattered by a surface and is crucial for understanding phonon-mediated thermal transport in low-dimensional semiconducting or insulating materials such as thin films and nanowires. However, there exists no reliable and accurate method to predict the relationship between the mode-dependent specularity parameter and the atomistic structure of a non-ideal edge or interface. [1] In addition, the dependence of the specularity parameter on wavelength, direction and polarization cannot be determined reliably with current theories.

To treat this problem, we introduce an S-matrix approach [2] that is grounded conceptually in conventional quantum mechanical scattering theory and developed from our earlier extension of the Atomistic Green’s Function (AGF) method, [3] allowing us to compute the scattering amplitude between an incident phonon and a reflected or transmitted phonon. The utility of our approach is illustrated through two example calculations. In the first example, we study the specularity dependence on edge chirality and explain how specularity is reduced for the ideal armchair edge in graphene, shedding light on the findings by Wei, Chen and Dames [4]. In the second example, we investigate grain boundary phonon scattering in graphene and provide direct evidence that the the specularity is significantly different between reflected and transmitted phonons. [5] Our S-matrix method resolves some of the existing difficulties in predicting the mode-dependent specularity parameter and opens the way for analyzing how edges and interfaces can be modified to control phonon scattering with atomistic precision.

References:

2:30 PM QN04.02.04
High-Throughput Thermal Conductivity Predictions and Spatial-Temporal Imaging Ding Ding$^{1}$ and Kedar Hippalgaonkar$^{2,3}$; $^{1}$Institute of Materials Research and Engineering, Singapore, Singapore; $^{2}$MSE, Nanyang Technological University, Singapore, Singapore; $^{3}$Singapore Institute of Manufacturing Technology, Singapore, Singapore.

With nanostructures in solid state materials reaching the size of the phonon mean free path and lower, quasilocalistic and anisotropic effects play significant roles in their thermal properties. Many new experimental techniques have been developed to probe phonon physics at such lengthscapes, however ascertaining spatially dependent thermal properties typically requires control of parameters in the spatial or frequency domain. Here, I will present our proposal for a one-shot optical pump-probe methodology that can potentially directly image both spatial and temporal temperature profiles. Coupled with a multi-parameter optimization of the heat diffusion equation, this technique can prove powerful in measuring anisotropic and quasilocalistic heat transport directly, serving as a high-throughput tool for screening of thermal properties. Coupled with first principles DFT calculations of the grunsen parameter and debye temperature of a large number of compounds extracted from Materialsproject.org, I will illustrate a vision of how machine learning can be used for prediction of desirable thermal properties.

3:00 PM BREAK

SESSION QN04.03: Phonons, Magnons and Magnetic Phenomena
Session Chairs: Chris Dames and Kedar Hippalgaonkar
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 124 A

3:30 PM *QN04.03.01
Research into magnetic devices – emerging memory, logic, and oscillator technologies – is enabled by magnetic imaging techniques that possess simultaneous picosecond temporal resolution and 10 – 100 nm spatial resolution. Conventionally, this combination is available only at facility-based research centers using e.g., pulsed x-ray dichroism techniques. In addition, many of the most exciting magnetic material systems, including ultrathin ferromagnetic or antiferromagnets insulators buried beneath heavy metals are difficult to image with any method. To address these challenges in a accessible way, we have developed a table-top spatiotemporal magnetic microscope based on nanoscale, picosecond thermal pulses. Our method takes advantage of magneto-thermal interactions that couple heat flow to electron or spin transport, including the anomalous Nernst effect [1] and the longitudinal spin Seebeck effect [2]. Using focused light as a picosecond heating source, we demonstrate that these imaging modalities have time resolution on the order of 10 ps and sensitivities to magnetization angle of 0.1 – 0.3°/Hz for ferromagnetic metals and insulators. In combination with phase-sensitive microwave current imaging, phase-sensitive ferromagnetic resonance imaging [3] enables direct imaging of the gigahertz-frequency magnetic driving torque vector, which is valuable for understanding spin-orbit interactions [4]. We also demonstrate magneto-thermal imaging of antiferromagnetic order in FeRh and NiO, offering a simple and accessible method to study spin-orbit torque switching of antiferromagnetic materials [5]. Finally, we will describe how time-resolved magnetic imaging can be extended to greatly exceed the optical diffraction limit, both theoretically [6] and experimentally. We demonstrate scanning a sharp gold tip illuminated by picosecond laser pulses as the basis of a nanoscale spatiotemporal magnetic microscope.

References:

4:00 PM QN04.03.02 Spin-Lattice Dynamics Calculations of Phonon-Magnon Coupling in Bulk Magnetic Materials Joseph Cooke and Jennifer R. Lukes; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

We present calculations of phonon-magnon coupling in bulk iron and nickel using spin-lattice dynamics [1,2], an increasingly popular simulation technique in which atomic spins and positions are computed simultaneously. It has been shown recently that a position-dependent magnetic anisotropy term is required to allow for full two-way coupling of thermal energy between the spin and lattice subsystems [3,4], but the parameters in this term are not known for many materials. Here we describe a procedure to obtain these parameters from experimental data on iron and nickel. We find that simulations including our parameters yield physically meaningful thermalization of spin and lattice systems and produce coupling times on the order of 100 ps, which agrees with the order of magnitude for coupling times reported by others [3,5].

References:

4:15 PM QN04.03.03 Effect of External Magnetic Field on Electron-Phonon Coupling and Transport Properties Jiayue Yang, Wenjie Zhang and Linhua Liu; School of Energy and Power Engineering, Shandong University, Qingdao, China.

With its merit of being controllable, nondestructive and easy-to-apply, magnetic field demonstrates great advantages in engineering electrical and thermal transport for practical applications. Yet, the scientific challenge is to better understand how the quantum behaviors of electrons and phonons that dominate the electrical and thermal transport respectively, are modulated by the external magnetic field. In this work, we apply the all-electron first-principles simulations to calculate the influence of external magnetic field on the intrinsic electron-phonon coupling, and then investigate its effect on the electronic thermal conductivity of representative metals (Al, Ni and Nb), superconducting transition temperature of hydrogen sulfide and magnetoresistance of monolayer WTe₂. For the electronic thermal conductivity study, the crucial issue is that electron-phonon coupling dominantly determines electron’s lifetime and external magnetic field can modulate electronic thermal transport by altering the electron-phonon coupling. We observe opposite change trend of electronic thermal conductivity with varying external magnetic field in Al, Ni and Nb, which is closely related to its electron localization function. Moreover, we find that magnetic field can slightly reduce the superconducting transition temperature of hydrogen sulfide and then modulates the thermoelectric properties of Al, Ni and Nb.

References:

4:30 PM QN04.03.04 Quasiparticle Thermometry in Nonequilibrium Systems Xiaoxin E. Li; University of Texas at Austin, Austin, Texas, United States.

In nonequilibrium phenomena, different quasiparticles such as phonons and magnons may exhibit different temperatures with the caveat that temperature is only strictly defined for an equilibrium system. Spin caloritronics, as an emerging field, investigates the interplay between the transport of spin and heat. In the representative spin Seebeck effect [1], a thermal gradient across a magnetic material generates a spin current. Many theories hypothesize that a temperature difference between the energy carriers of the spin and lattice subsystems, namely the magnons and phonons, is necessary for such thermal nonequilibrium generation of spin current. The experimental evidence for such phonon-magnon nonequilibrium has been critically lacking [2] because of the difficulty to characterize phonon and magnon temperatures independently.

We use Brillouin light scattering (BLS) to investigate thermally driven spin current in a prototypical magnetic insulator yttrium iron garnet (YIG). BLS, as an inelastic light scattering technique, is conceptually the same as Raman scattering. It is optimized to probe low-frequency excitations, e.g., acoustic phonons and magnons. These quasiparticles are the main energy and spin carriers in magnetic insulators. Three different quantities (i.e., central frequency, linewidth, and integrated intensity) associated with the BLS spectra are the main energy and spin carriers in magnetic insulators. Three different quantities (i.e., central frequency, linewidth, and integrated intensity) associated with the BLS spectra all vary with temperature systematically and can be used as a temperature sensor for probing phonons and magnons independently [3]. We show how BLS spectra can be used to probe phonon-magnon non-equilibriums [4], measure pure spin current, and evaluate magnon chemical potential in a magnetic insulator thermally driven out of equilibrium.

References:
Scanning Thermal Microscopy (SThM) allows the thermal characterization of materials with a submicrometric spatial resolution [1]. While obtaining qualitative trends, e.g. by means of maps, is straightforward, determining reliable quantitative thermal data from the experiments is challenging because the probe-sample heat exchange depends strongly on parameters such as the size, geometry and surface states of probe and sample [2-3]. There is a need for a complete and accurate thermal measurement methodology, which is the aim of this work. We focus on heated probes dissipating heat flux into samples initially at ambient temperature. Simultaneous heating and measurement of the SThM probe temperature provide information on the sample effective thermal conductivity.

For three different electrically-resistive and Joule-heated SThM probes, involving different sizes and sensor materials (etched Wollaston-wire microprobe, palladium nanoprobe and doped silicon nanoprobe), an improved methodology for thermal conductivity local-point measurement was developed. Studies in ambient and vacuum conditions were considered. The methodology enables to eliminate the impact of thermal drifts occurring in such experiments, to deal with the variation in the laser irradiation on the cantilever and probe, and to detect any change at the tip apex due to a deformation or a contamination. As a consequence, results are reproducible with a temperature resolution of the order of few millikelvins.

Specimens of well-known thermal conductivity spanning between 0.1 and 150 W.m⁻¹.K⁻¹ and surfaces controlled in terms of roughness and nanomechanical properties were used as reference materials in order to obtain a calibration curve for each probe. In the three cases, their applications allow us to clearly confirm that thermal-conductivity measurements with SThM are limited to low thermal conductivity materials (k < few W.m⁻¹.K⁻¹). This is due to the designs of the cantilever of the three probes and may not easily be improved. As expected, reducing the probe size and placing it in vacuum improves the spatial resolution, but it also induces unfortunately an increase of sensitivity to the tip-sample contact physical parameters (e.g. roughness, thermal boundary resistance, surface state), which is detrimental to the accuracy.

The impact of roughness on the thermal conductance at the contact was studied in detail. Samples consisting of several sets of silicon surfaces with out-of-plane Sq roughness parameters of ~0.5, 0.4, 4, and 12 nm were prepared by anodic oxidation [5]. Our results show that roughness induces a thermal conductance decrease at the contact up to 35% compared to a flat silicon sample, depending on the probe and environment. Precise knowledge of the surface state is therefore key to accurate measurements.

The calibration and methodology were applied to characterize thin films of oxides and materials involved in electronics. The experimental results are backed by finite-element simulations (FEM) including effective thermal conductivities when the size requires it, local heat sinks representing thermal constrictions of typical sizes smaller than the energy carrier mean free paths (when FEM is not able to capture the correct physics), and thermal boundary conductances in the Acoustic or Diffuse Mismatch Models (AMM-DMM). Advantages and drawbacks of SThM are discussed in light of the results.


The research leading to these results has received funding from the EU FP7 Programme under GA n°604668. and French ANR Programme under project TIPTOP.
while angstrom-scale responses can be tracked in reciprocal space. In UEM, as in other ultrafast electron and X-ray experiments, the Debye-Waller (DW) effect is often invoked when explaining photoinduced scattering intensity changes and when determining transient temperatures by relating the changes to atomic thermal vibrations. While this enables direct probing of the intrinsic lattice response to thermal effects with high spatial and temporal resolutions, reliance on transient intensity changes of diffracted beams poses significant challenges. This is because factors other than mean-square atomic displacements can produce signal changes similar to those generated by thermal effects [3-5]. Therefore, in order to accurately and precisely determine nanoscale transient temperatures using ultrafast scattering methods, deleterious effects that obfuscate intensity changes arising from atomic thermal vibrations must be identified, quantified, and deconvolved.

To address this, we have systematically studied and quantified a number of potential effects that can arise during in situ fs photoexcitation that may impact DW-type responses and the resulting interpretations [6]. Using small-grained polycrystalline aluminum films as a well-characterized test system, we explicitly illustrate the impact of specimen tilting and translation via rigorous statistical analysis of Debye-Scherrer-ring intensities obtained from numerous individual specimens and measurements. Despite having more than 10⁶ individual grains within the selected areas, we find that tilting by as little as a fraction of a degree, or translating a 22.5-μm diameter illuminated region by only 20 nm, yields statistically-significant changes in the diffracted-beam intensity. This result is at first surprising, as one may have expected a uniform distribution of random zone-axis orientations under such conditions, thus circumventing any negative effects due to specimen tilting and translation. We explicitly show this is not the case, and we explore and quantify several sources of error and artifacts, such as slight texturing of the polycrystalline films due to surface-energy minimization. Possible approaches to mitigating inaccuracies in the DW-calculated temperatures are also addressed, including effective methods of data normalization and consideration of ideal specimen geometries for such studies.


QN04.04.04
Correlating Coherent Structural Dynamics to Photoexcited Charge-Carrier Behaviors Using Femtosecond Electron Imaging

Daniel Del¹; Daniel R. Cremons¹,² and David J. Flannigan¹
¹University of Minnesota Twin Cities, CEMS, Minneapolis, Minnesota, United States; ²NASA Goddard Space Flight Center, Greenbelt, Maryland, United States.

Intense femtosecond (fs) photoexcitation of semiconducting materials can lead to the generation of high densities of charge carriers, shifting the Fermi-Dirac distribution into a highly non-equilibrium state. The relaxation pathways available to this new state are numerous, and the associated mechanisms can be intermingled and highly non-linear [1]. One particular pathway is via the excitation of highly-coherent, low-frequency acoustic phonons that propagate outward from the photoexcited zone [2]. For initially high carrier concentrations, this behavior is attributed either to a time-varying deformation potential or a time-varying thermoelastic effect, depending upon the band structure and the nature of photoexcitation. Importantly, these two regimes can be differentiated temporally, depending upon the carrier densities generated; at relatively high concentrations, Auger recombination begins to further augment the time-varying thermoelastic effect. Indeed, a material as simple as undoped germanium (Ge) displays several intriguing transient behaviors within the context just described. For example, the excited carrier-density lifetimes can be quite long and can significantly overlap with the electron-phonon coupling times, thus heavily interweaving the various relaxation pathways [3,4]. Further, intense fs photoexcitation can lead to the generation of hypersonic electron-hole plasma waves, the nature of which may evolve into coherent acoustic-type oscillatory behaviors [5]. This suggests such behaviors may manifest as coherent, transient lattice-strain effects, the properties of which are directly linked to the hypersonic plasma waves [6].

Here, we describe our efforts to link the photoexcited charge-carrier dynamics in single-crystal Ge to the lattice degrees of freedom using fs electron imaging in an ultrafast electron microscope [7,8]. By leveraging the extreme sensitivity of local diffraction contrast to changes in reciprocal-lattice orientation, we are able to directly image the generation and the evolution of highly-coherent acoustic phonons initially propagating at hypersonic velocities in the plane of the crystal [9]. While each phonon wavefront propagates with a constant velocity, the entire wave train displays a time-varying phase-velocity dispersion, relaxing from initial velocities greater than 35 nm/s to the Ge longitudinal speed of sound (5 nm/ps) within one nanosecond. Analysis of the dispersion curves expected for symmetric dilatational and asymmetric flexural modes indicates the dynamics match most closely to a single, low-order symmetric mode. Interestingly, this symmetric mode appears to give rise only to increased scattering for each wavefront, indicating the reciprocal-lattice shapes (approximated here as rods) are only brought further onto the Ewald sphere rather than being equally distributed during the oscillation. Further, by using a plasma lensing technique [10], we find that the onset of the first phonon wavefronts are delayed by tens of picoseconds or more, relative to the moment of fs photoexcitation. Combined, these anomalous behaviors provide tantalizing hints of charge-carrier-dominant dynamics, rather than lattice deformations caused by coherent phonons, as producing the observed ultrafast contrast behaviors. Those possibilities are explored here.


QN04.04.05
Thermal Transport in Holey Silicon Membranes Investigated with Optically-Induced Transient Thermal Gratings

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In semiconductor nanostructures with feature sizes on the order of 100 nm, thermal transport is expected to be well-described by the phonon Boltzmann transport equation (BTE) with diffuse boundary scattering. However, over the past several years there have been reports of anomalously low effective thermal conductivity values in one- and two-dimensional semiconductor nanostructures. In this study, we investigate thermal transport in nanostructured holey silicon membranes using the non-contact optical transient thermal grating (TTG) technique. We compare the experimental results with two ab-initio BTE numerical techniques. We obtain excellent agreement between theory and experiment, indicating that semi-classical Boltzmann transport theory for phonons is adequate for describing room-temperature thermal transport in semiconductor nanostructures with feature sizes on the order of 100 nm.

QN04.04.06
Theory of Anisotropic Thermal Interface Resistance in Nanocomposite Materials

Iorwerth O. Thomas and Gyaneshwar P. Srivastava; University of Exeter, Exeter, United Kingdom.

We present a theory of anisotropic thermal interface (Kapitza) resistance for rough interfaces in nanocomposite materials. This is based on an extension [1] of a modified effective medium theory [2,3] that includes anisotropically resistive interface regions in a model of the lattice thermal conductivity of anisotropic nano insertions in anisotropically conductive hosts. The thermal conductivities of the host and nanodot insertions have been evaluated using a semi ab-initio theory [4] based on the solution of the linearised phonon Boltzmann transport equation within a generalized [5] Callaway effective relaxation time scheme [6]. Phonon boundary scattering and the Kapitza resistance at the insertion-host interface have been treated by taking into account both specular and diffuse contributions [7,6]. The theory has been applied to a transition metal dichalcogenide (TMD)
nanocomposite consisting of 2H WS2 inserts in a 2H MoS2 host. In general, it is found that the effect of specular scattering due to interface roughness is more pronounced for inserts smaller than 100 nm. Analysis of the results allows us to identify key physical parameters that should prove effective in controlling (i.e. obtaining minimum) lattice thermal conductivity of TMD nanocomposites.


**QN04.04.07**

**Impact of Irradiation Induced Nanoscale Defects on Thermal Conductivity of Cerium Dioxide**

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Thermal conductivity is a critical physical property of ceramic nuclear fuels such as uranium dioxide. While cerium dioxide is considered as a solid electrolyte in solid oxide fuel cells (SOFC), in this study it is used as surrogate material to study the properties of nuclear fuel. In nuclear fuel, these oxides are exposed to extreme environments such as high temperature and bombardment with heavy particles. The damage introduced by such conditions in the form of defects generated inside the material can be detrimental to the structural stability of the material and ability to transport heat efficiently. Also, thermal conductivity degradation impacts fuel performance negatively. As a result, thermal conductivity of ceria has been widely investigated as one of the critical properties. This study is aimed at understanding the interplay between these nanoscale defects and the thermal conductivity of ceria.

Polycrystalline ceria samples were irradiated at 600 deg C to the same dose but at different rates using protons accelerated to 2 MeV. These irradiation conditions were chosen to promote the generation of nanoscale defects and to investigate their impact on thermal conductivity of ceria. SRIM simulations were done to identify the peak and plateau damage region inside the sample. The calculations estimated the plateau damage to be ~0.14 dpa. The quantitative analysis of radiation induced dislocation loops including size and density was performed using transmission electron microscope (TEM) for which the samples were prepared using focused ion beam (FIB) system.

X-ray diffraction was used to confirm the stability of the crystal structure and also revealed detectable lattice expansion caused by accumulation of nanoscale defects. In addition to this, thermal conductivity was measured using modulated thermoreflectance methods and showed a notable reduction in irradiated samples. In order to isolate the impact of different defects on thermal conductivity, measurements were done for ambient temperature range of 100 to 300 K. The changes in thermal conductivity were analyzed quantitatively using the classical thermal transport model based on Klemens-Callaway formalism that considers reduction of thermal conductivity by irradiation induced nanoscale defects.

**QN04.04.08**

**Multiscale Thermal and Electrical Modeling of CMOS Devices and Circuits**

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This simulation work explores the thermal effects on electrical characteristics of CMOS devices and circuits using a multiscale dual-carrier approach. Simulating for electron and hole transport simultaneously allows for complimentary logic gates to be simulated at the device level, while current and voltage continuity are maintained at the circuit level. Further, the electrical model couples with a multiscale thermal solver, which solves for electron-phonon and hole-phonon interactions at the device level and phonon-phonon thermal transport in the packaging level. This methodology allows for the study of package level thermal transport without sacrificing the nuances of device self-heating, ultimately providing a more comprehensive understanding of how these interactions affect power consumption in CMOS systems.

The electrical model is comprised of an ensemble Monte Carlo simulator coupled with a Poisson solver. This framework provides accurate electrical characteristics in quasi-static regimes by iteratively solving for the potential profile and the electric fields then simulating the effect of the electric field on charge carriers. The Monte Carlo simulator solves the Boltzmann Transport by balancing each particle’s movement in real and momentum space with the collision integral through probabilistic scattering mechanisms. This framework provides current and voltage characteristics for each device; current and voltage continuity are maintained by solving at the circuit level.

Similarly, the methodology for simulating thermal characteristics includes two scales. At the device scale, the energy balance equation determines the transfer of energy from charge carriers to phonons. High-energy electrons or holes relinquish energy to optical and acoustic phonons through scattering and optical phonons decay into acoustic phonons. At the package level, a Fourier law solver simulates the subsequent conduction of heat in the form of lattice vibrations.

This framework proved effective in previous simulations for the electro-thermal characteristics in NMOS devices. This work demonstrates the effectiveness of the dual-carrier electrical solver in simulating CMOS circuits. Future work requires the coupling the dual-carrier electrical solver with the previously proven thermal solver to provide comprehensive electro-thermal simulations of CMOS systems.

**QN04.04.09**

**Graphene Composites for Thermal and Electromagnetic Shielding Applications—Performance Below and Above Percolation Thresholds**

Fariborz Kargar, Zahra Barani, Jacob S. Lewis, Ruben Salgado, Sahar Naghibi, Ece Aytan and Alexander A. Balandin; Phonon Optimized Engineered Materials (POEM) Center, Department of Electrical and Computer Engineering, Materials Science and Engineering Program, Bourns College of Engineering, University of California, Riverside, Riverside, California, United States.

Excellent heat conduction properties of graphene and the progress in the large-scale few-layer graphene exfoliation make the prospects of graphene composite applications particularly promising [1-2]. We investigated thermal properties of the epoxy-based composites with a high loading fraction – up to 45 vol. % – of the randomly oriented electrically conductive graphene fillers and electrically insulating boron nitride fillers [3]. It was found that both types of the composites revealed a distinctive thermal percolation threshold at the loading fraction above 20 vol.%. The graphene loading required for achieving the thermal percolation was substantially higher than the loading for the electrical percolation. Graphene fillers outperformed boron nitride fillers in the thermal conductivity enhancement. It was established that thermal transport in composites with the high filler loading is dominated by heat conduction via the network of percolating fillers. Unexpectedly, we determined that the thermal transport properties of the high loading composites were influenced strongly by the cross-plane thermal conductivity of the quasi-two-dimensional fillers. It was also found that composites with the certain types of few-layer graphene fillers reveal an efficient total electromagnetic interference shielding in the important X-band frequency range, while simultaneously providing the high thermal conductivity [4]. The efficiency of the dual functional application depends on the filler characteristics: thickness, lateral dimensions, aspect ratio and concentration. Graphene loading fractions above the electrical and thermal percolation thresholds allow for strong enhancement of both the electromagnetic interference shielding and heat conduction properties. Interestingly, graphene composites can block the electromagnetic energy even below the electrical percolation threshold, remaining electrically insulating. The dual functionality of the graphene composites can substantially improve the electromagnetic shielding and thermal management of the airborne systems while simultaneously reducing their weight and cost.

This work was supported, in part, by the National Science Foundation (NSF) through the Emerging Frontiers of Research Initiative (EFRI) 2-DARE award 1433395, and by the University of California – National Laboratory Collaborative Research and Training Program LFR-17-477237.

loading of graphene and boron nitride fillers,” ACS Applied Materials and Interfaces, (2018) DOI:10.1021/acsami.8b16616.


QN04.04.10 Fine-Tuning the Acoustic Phonon Spectrum in Bulk Crystals via Incorporation of the Size-Dissimilar Substitutional Dopant Atoms—Brillouin—Mandelstam Spectroscopy Study Fariborz Kargar1, Elias H. Penilla2, Chun-Yu T. Huang1, Ece Aytan1, Javier E. Garay2 and Alexander A. Balandin1; 1Phonon Optimized Engineered Materials (POEM) Center, Department of Electrical and Computer Engineering, Materials Science and Engineering Program, Bourns College of Engineering, University of California, Riverside, Riverside, California, United States; 2Advanced Materials Processing and Synthesis (AMPS) Laboratory, Department of Mechanical and Aerospace Engineering, University of California, San Diego, San Diego, California, United States.

Acoustic phonons make a dominant contribution to thermal transport in insulators and semiconductors, scatter electrons and holes, and participate in the non-radiative carrier recombination processes. Acoustic phonons are important in certain types of the Auger recombination processes where they are needed to satisfy the momentum conservation. A possibility of engineering the acoustic phonon spectrum provides a tuning capability for changing thermal conductivity and electron – phonon interactions [1]. Until recently, the tuning of the phonon spectrum has been associated with the nanostructured materials, where the phonon dispersion undergoes modification due to the periodic or stationary boundary conditions. In this talk, we describe a drastically different approach for changing the acoustic phonon spectrum of the materials, which does not rely on nanostructuring [1]. We change the phonon spectrum in bulk crystalline materials via introduction of a small concentration of dopant atoms that have a substantially different size and mass from those of the host atoms. We report results of Brillouin – Mandelstam spectroscopy (BMS) of transparent Al2O3 crystals with Nd, Cr and other atoms used as substitutional dopants. The ionic radius and atomic mass of Nd atoms are distinctively different from those of the host Al atoms. Our results show that even a small concentration of Nd atoms incorporated into the Al2O3 samples produces a profound change in the acoustic phonon spectrum. The frequency and velocity of the transverse acoustic phonons decrease by ~4 GHz and ~600 m/s, respectively, at the Nd density of only ~0.1 %. In contrast to Nd dopants, both the ionic radius and atomic mass of Cr atoms are closer to those of the host Al atoms. The BMS results show that the phonon group velocity does not significantly change when the substitutional dopants are similar in size and mass to the host atoms. Our findings confirm that even a small concentration of dopants with strongly dissimilar size and mass can result in a profound change in the bulk phonon spectrum. The difference in atomic size can result in the crystal lattice distortion, i.e. increased inter-atomic plane distance associated with the incorporation of larger atoms. The obtained results, demonstrating a possibility of fine-tuning the phonon spectrum in bulk materials, have important implications for a range of electronic and optoelectronic devices. This work was supported, in part, by the Spins and Heat in Nanoscale Electronic Systems (SHINES), an Energy Frontier Research Center funded by the US. Department of Energy, Office of Science, Basic Energy Sciences (BES) under Award # SC0012670. AAB acknowledges support from the Defense Advanced Research Projects Agency (DARPA) project W911NF-18-1-0041 Phonon Engineered Materials for Fine-Tuning the G-R Center and Auger Recombination. JEG acknowledges support from the High Energy Laser - Joint Technology Office (HEL-JTO) administered by the Army Research Office for development of over-equilibrium doped alumina.


QN04.04.11 Electron-Phonon Coupling in Metal Contacts—Two-Temperature Molecular Dynamics Simulations Henry Aller, Jonathan A. Malen and Alan McGaughey; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

The interface between a metal and a semiconductor that have dissimilar phonon frequency spectra typically exhibits a low thermal boundary conductance, as found for many Au/semiconductor interfaces. A thin metal layer (i.e., a contact or adhesion layer) placed between the gold (i.e., the capping layer) and the semiconductor can increase the thermal boundary conductance, an effect that has been attributed to the contact serving as a vibrational bridge. The impact of a change in the electron-phonon coupling due to the presence of the contact on the thermal boundary conductance, however, is not fully understood. To assess the roles played by vibrational bridging and electron-phonon coupling, we apply a two-temperature non-equilibrium molecular dynamics simulation approach. By specifying the heat flow through a structure, we can predict the temperature profiles in the electronic and phononic subsystems and the resulting thermal boundary conductance(s). Four types of structure built from metals (M) and semiconductors (SC) are considered: M/M, M/SC, M/SC/SC, and SC/SC/SC. Increasing the contact layer thickness for the M/MS/SC systems results in a monotonic increase in thermal boundary conductance, matching trends from previous experimental studies. The phonon density of states in the contact layer identifies the existence of non-bulk phonon modes for small thicknesses. Increasing thickness results in contact layer phonons gradually shifting to bulk frequencies, which explains the occurrence of the plateau in thermal boundary conductance for large thicknesses. A comparison between the M/M/SC, M/SC/SC, and SC/SC/SC systems provides insight to how the electron-phonon coupling in each metal layer impacts thermal boundary conductance.

QN04.04.12 Extending the Lattice Boltzmann Phonon Transport Approach Towards the Ballistic Regime Natalia Bedoya-Martinez, Verena Fritz and René Hammer; Materials Center of Leoben, Leoben, Austria.

The thermal conductivity is a system property rather than a material property alone, i.e. the mechanisms that govern the thermal conductivity strongly depend on the system (e.g. length scale, phonon confinement, ballistic interface and boundary effects). A specific model, then, capable to account for the different mechanisms should be used. Among the different models to study thermal transport, the most standard one is based on the Fourier’s law, which can be implemented either in the framework of classical or ab-initio molecular dynamics (MD) simulations. MD builds on classical Newton’s equation of motion and, therefore, does not account for nuclear quantum effects that are present below the Debye temperature [1]. Furthermore, ab-initio and MD simulations may feature strong size effects due to the limited size of the computational domain. Fourier’s law based models, thus, do not properly account for the ballistic, wave like, and quantum phenomena of heat transport.

At a length scale, L, of the order of the phonons mean free path, λ, a statistical description of the phonon transport using the Boltzmann transport equation is required (e.g. 50% of thermal conductivity in bulk silicon at RT comes from phonons having mean free paths > 500 nm [2]). This, however, is very demanding from a computational point of view. Even new developments (e.g. energy based and deviational formalism [3]) in stochastic Monte Carlo methods, are still too expensive to simulate 3D device problems on standard workstations. Deterministic methods for solving the phonon Boltzmann transport equation, on the other hand, suffer from ray effect and / or false scattering [4]. These effects strongly limit their accuracy in the high Knudsen number regime (i.e. λ<< L).

Here, we present a set of improvements on the lattice Boltzmann method (LBM), in order to extend its applicability far into the ballistic regime. First of all, we get rid of the numerical boundaries by allowing adaptive time steps. This allows us to go beyond the grey approximation (i.e. average phonon properties), and to introduce several phonon species with different group velocities on one grid. Secondly, we go beyond the next neighbour hopping for the LBM stencil. This allows to increase the number of discretized directions (e.g. to reduce the ray effect) without introducing false scattering. The new numerical algorithms are applied to standard 2D transient and stationary phonon heat transport cases, with different group velocities on one grid. Secondly, we go beyond the next neighbour hopping for the LBM stencil. This allows to increase the number of discretized directions (e.g. to reduce the ray effect) without introducing false scattering. The new numerical algorithms are applied to standard 2D transient and stationary phonon heat transport cases, and are benchmarked against analytical and numerical solutions given by the discrete ordinate method and MC simulations.


QN04.04.13 Thermal Conductivity of CuSn Matthias A. Daemuel1, Arad Azzii2, Sitaram Pant2, Faramarz Hadian2, Eric J. Cotts3 and Scott N. Schiffres4; 1Mechanical Engineering, Binghamton University, Bing, New York, United States; 2Department of Physics, Binghamton University, The State University of New York, Binghamton, New York, United States.

In order to realize vertical integration for next generation electronics packaging, purely intermetallic bonding is a promising contender to replace solder. The thermal properties of these industrially important intermetalities are relatively unstudied and poorly understood. Due to their high melting temperatures intermetallics bonds provide stability through
several refinements enabling vertical packaging. However, in vertical packaging the interconnects must carry a significant portion of the heat away from the chip. In an effort to better understand the thermal capability of fully intermetallic bonding Frequency Domain Frequency Domain Thermoreflectance mapping was used to determine thermal conductivity of the arc-melted CuSn with respect to crystallographic orientation. This will be complemented by electron backscatter diffraction mapping of the crystal orientation.

QN04.04.14
Uncovering Phonon Transport Mechanisms Underneath Nanoscale Heat Sources Hossein Honarvar1, 2, Joshua Knobloch1, Travis D. Frazer1, Jorge Nicolas Hernandez Charpak1, Begona Abad Mayor1, Mahmoud I. Hussein2, Henry Kapteyn1 and Margaret Murnane1; JILA/Physics, University of Colorado Boulder, Boulder, Colorado, United States; 1Aerospace, University of Colorado Boulder, Boulder, Colorado, United States.

Nanostructured and quantum materials are enabling revolutionary advances in nanoscience and nanotechnology. These engineered materials promise to go beyond what is offered by natural materials. Advances in materials growth now make it possible to synthesize 3D nanostructured materials with nanometer resolution creating nanosystems with tunable electronic, electronic, photonic, magnetic, and thermal properties for a variety of applications including nanoelectronics, thermoelectrics, photovoltaics, and sensors. However, understanding of the fundamental mechanism behind many of these applications is still incomplete, making the development of powerful theoretical and experimental tools a priority for many material research communities.

Understanding thermal transport in nanostructured systems has long been a challenge. In the last few years, experimental techniques have pushed the measurement limits on systems with characteristic dimensions and geometries down to tens of nanometers, often times finding new surprising physical behaviors [1]. However, it is still challenging to apply appropriate models that connect novel data to meaningful thermal properties and fundamental mechanisms. Most researchers rely on using effective or phenomenological diffusive models or the linearized Boltzmann transport equation that are not able to capture all of the observed nanoscale effects and nonlinear interactions [1-3]. This is because it is very difficult to perform atomistic simulations over experimentally-relevant length scales, due to prohibitive computational requirements. As a result, there is a large gap in understanding of how the nanoscale phonon physics unfold for different size and geometries to modify the transport properties. Moreover, possible coherent effects are often not adequately included in current models.

The focus of this work is understanding thermal transport in nanostructured materials by bridging the gap between theory and experiment. In particular, previous work done in our research group uncovered a new thermal transport regime named “collectively-diffusive” by tracking the heating and cooling of periodic arrays of nanoscale heat sources on bulk crystalline silicon and sulphide substrates [1]. This regime emerges from the interaction between the nanoscale geometries and energy carriers in materials. In particular, when nanoscale heat sources are placed closer, they cool down faster than when farther apart—the opposite of heat dissipation dynamics of the macroscale. The observed increase in heat dissipation efficiency has large consequences in thermal management in microelectronic devices, and is currently not captured by models available to both researchers in academia and industry. In this work, we present the results of steady-state molecular dynamics (MD) simulations that can model the experimentally-explored geometries, and how these results provide a global understanding of non-diffusive phonon dynamics that appear to dominate energy transport in the deep nanoscale regime. Our MD results of nanoscale heat sources indicate that we are able to successfully capture the novel collectively-diffusive thermal dynamics observed recently.


QN04.04.15
Thermal Conductivity of Perovskite-Structured Superlattices from First-Principles Calculations Qi Zhang1, Xue Xiong2, Eugene Rasaga2, Simon Phillip2 and Aleksandr V. Chernyatsky1; 1Physics, Missouri University of Science and Technology, Rolla, Missouri, United States; 2Material Science and Engineering, University of Florida, Gainesville, Florida, United States.

Low thermal conductivity materials are important for a variety of applications, including thermal barrier coatings and thermoelectric devices. Superlattices are particularly interesting due to the possibility of lowering thermal conductivity. Numbers of explanations have been proffered for the low thermal conductivity of superlattice structures. A full explanation, however, has yet to be developed. Here, we are presenting the thermal transport properties of natural perovskite-structured superlattices, the Ruddlesden-Popper (RP) series of phases of the Sr-Ti-O system, formed by the interleaving of SrTiO3 perovskite layers with SrO rocksalt layers. We have computed their thermal conductivity from first principles via the Boltzmann-transport equations (BTE) approach encoded in the PhonTS software package. In short, the thermal conductivity is determined by computing the heat current using the nonequilibrium phonon density distribution function, which in turn is found as a solution of the linearized BTE for phonons. The required input for the BTE are the second and third spatial derivatives of the total energy with respect to atomic positions which we have obtained from the DFT calculations performed using the Vienna Ab initio Simulation Package (VASP) computational package. A clear minimum in the thermal conductivity as a function of a number of STO layers is observed. Results are compared with the recent experimental data.

QN04.04.16
Controlling Thermal and Electrical Properties of Composites Using Percolating Network of Nanowires with Fusible Tips Konrad Rykaczewski and Robert Wang; Arizona State University, Tempe, Arizona, United States.

Development of polymer composites with high thermal conductivity is necessary for thermal management of microelectronics. Percolation of metallic filler particles and reduction of the thermal contact resistance between individual particles (e.g. via thermal or electromagnetic fusing) can significantly improve thermal conductivity of composites. However, composite materials with connected metallic particles can also conduct electricity, creating a risk of short-circuiting in chip-board and the inter-chip gaps. In this presentation we theoretically show that this can be resolved with the application of fusible metallic coatings to the tips of nanowires with thermally conductive, but electrically insulating cores [1]. Specifically, we use Monte Carlo simulation-validated analytical models that relate the ratio of the coated and total nanowire lengths to the fraction of fused, and thus conductive, bonds within percolating networks of these structures to show that thermally conductive, but electrically insulating composites can be achieved using these novel nanowire structures. We discuss silver-like coatings, which only form conductive bonds when contacting the silver-like coating of another nanowire as well as liquid metal-like coatings, which form conductive bonds regardless of whether they contact a coated or uncoated segment of another nanowire. We show that use of the liquid metal-like coatings will yield twice as many thermally conductive bonds as silver-like coatings while maintaining a negligible risk of electrical short-circuiting.


QN04.04.17
Magnon and Phonon Dispersion, Lifetime and Thermal Conductivity of Iron from Spin-Lattice Dynamics Simulations Zeyu Liu1, Xufei Wu1, 2; 1Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana, United States; 2Center for Sustainable Energy (ND Energy), University of Notre Dame, Notre Dame, Indiana, United States.

In recent years, the fundamental physics of spin-lattice (e.g., magnon-phonon) interaction has attracted significant experimental and theoretical interests given its potential paradigm-shifting impacts in areas like spin-thermoelectrics, spin-caloritronics, and spintronics. Modelling studies of the transport of magnons and phonons in magnetic crystals are very rare. In this paper, we use spin-lattice dynamics (SLD) simulations to model ferromagnetic crystalline iron, where the spin and lattice systems are coupled through the atomic position-dependent exchange function, and thus the interaction between magnons and phonons is naturally considered. We then present a method combining SLD simulations with spectral energy analysis to calculate the magnon and phonon harmonic (e.g., dispersion, specific heat, and group velocity) and anharmonic (e.g., scattering rate) properties, based on which their thermal conductivity values are calculated. This work represents an example of using SLD simulations to understand the transport properties involving both magnon and phonon dynamics.

QN04.04.18
Normal Modes for Thermal Transport Anup Rai and Jacob Eappen; North Carolina State University, Raleigh, North Carolina, United States.

Normal modes of vibrations can be extracted from atomistic simulations by projecting the real space trajectories onto the reciprocal space. Normal modes coordinates are not
unique and their primary function is to transform the coupled Hamiltonian to a set of independent harmonic oscillators. Several descriptors of normal modes exist but not all of them are appropriate for analyzing thermal transport. In most normal mode analyses (NMA), complex normal mode coordinates are employed, which combine the modal contributions of waves moving in opposite directions. The wave-vector \( q \) that is represented in the complex normal modes does not uniquely represent a wave traveling in the \( +q \) or \( -q \) direction, instead it denotes an average of both directions. Thus the popular complex normal modes have a theoretical inability to resolve a real heat current along a specific direction-dependent wave-vector \( q \).

In this work, we employ a set of real asymmetric normal mode coordinates, which can distinguish lattice waves moving in opposite directions – a virtue that immediately endows the ability to discriminate a heat current in a certain direction. These normal mode coordinates have a real amplitude \( A(q_p) \) that is not equal to \( A(-q_p) \). We then derive an expression for heat current that is real, and which can be expressed as a difference between the squares of the amplitudes in \( +q \) and \( -q \) directions. Finally, we drive a correction term for phonon lifetime that arises from the correlation between modes moving along opposite directions.

QN04.04.19

Recent experiments have evidenced that effective Fourier models are unable to predict heat transfer at the nanoscale [1,2]. This has a big impact on electronic engineering that relies on this law to study the thermal behavior of their devices.

One of the last proposals to better describe thermal transport at the nanoscale has been phonon hydrodynamics. In this line, the Guyer-Krumhansl equation has been proposed as the required generalization of the Fourier law to describe heat transport at this scale [3]. This equation is combined with the Kinetic Collective Model (KCM) to obtain the included parameters from ab initio calculations [4,5]. One of the main advantages of this approach is that its simplicity allows to obtain solutions for arbitrary geometries using Finite Element Methods. Therefore, this combination offers a full predictive framework to describe thermal conductivity in semiconductors in general geometries with characteristic sizes up to the order of the hybrid thermal characteristic length.

Validation of the model has been done with experimental data for different systems such as semiconductor porous membranes with different periodic alignments, thin membranes with different constrictions or 2D materials. In parallel, the tool offers also the interpretation of the results in terms of new phenomena like vorticity and viscosity, giving an insight on the reason for the reduction of the effective thermal conductivity at reduced scales.

References:

QN04.04.20
Effect of Intrinsic and Extrinsic Defects on Phonon Heat Transfer in Nanostructured Metals Peter V. Sushko, Richard Williams, Christopher Barrett and Marvin Warner; Pacific Northwest National Laboratory, Richland, Washington, United States.

Ongoing efforts in low temperature experimental research, including the work on quantum materials and high energy physics experiments, underscores the need to achieve and maintain ultra-low temperatures. Of particular interest are metal-non-metal systems, in which the dominant mechanism of heat transfer switches at the interface, and nanomaterials, in which structural and chemical deviations from idealities may lead to significant deviations from the Fourier law.

We investigate how phonon component of the heat flux across nanoscale metals is affected by point defects, dislocations and model two-dimensional defects. Gaseous models for the heat source and heat sink are adopted and the computations are conducted using classical molecular dynamics approach. Analysis of the heat transfer coefficients, as derived via Green-Kubo relation, suggests that surface nanopatterning and chemical defects have larger an effect on the heat propagation than intrinsic defects.

QN04.04.21
Thermal Transport Across Rough Interfaces — A Finite-Difference Time-Domain Study Laleh Avazpour, Sina Soleimankahnoj, Suraj Suri and Irena Knezic; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Heat transport across interfaces in nanostructures is an important open problem that arises into play in the design and operation of electronic and thermoelectric devices. In particular, lattice mismatch across the interface and the interface profile strongly influence thermal transport. In this work, we study elastic-wave scattering at the junction between two different materials. We solve the elastic-wave equations with the finite-difference time domain (FDTD) technique. We investigate the effects of mode conversion and energy trapping at the interface and how they are affected by interface roughness and lattice mismatch. The results provide a unique outlook on the interfacial heat transport and its effect on the operation of nanodevices.

QN04.04.22
Thermal Conductivity of Small-Angle Misoriented Bilayer Graphene Chenvang Li, Bishwajit Debnath and Roger Lake; Electrical and Computer Engineering, University of California, Riverside, Riverside, California, United States.

The properties of misoriented bilayer graphene have recently received renewed interest after the discovery of superconductivity at very small rotation angles. Compared to the electronic properties, the effect of misorientation on the phonon and thermal properties has received less attention. For the larger misorientation angles, the in-plane thermal conductivity depends not on the angle, but on the commensurate lattice constant, and the thermal conductivity decreases approximately linearly as the commensurate lattice constant increases [1]. This trend is qualitatively consistent with the hypothesis that the zone folding gives rise to an increase in Umklapp scattering that reduces the low-energy phonon lifetimes and thus the thermal conductivity. However, our recent calculations show that as the misorientation angle falls below 13.2°, this trend reverses itself, and the thermal conductivity starts increasing back towards the value of the unrotated structure. For angles below 13.2°, the thermal conductivity initially increases rapidly as the angle decreases from 13.2° to 7.3°, even though the commensurate lattice constant is monotonically increasing. As the angle continues to decrease down to 1.9°, which is the smallest angle simulated, the thermal conductivity gradually returns to its unrotated value.

For small angles with minimal commensurate unit cells, the commensurate lattice constants monotonically increase as the angles decrease, so that it is not clear what determines the functional dependence of the thermal conductivity in the small angle regime. Is it the misorientation angle or the commensurate lattice constant? To answer this question, we investigated two very different angles, 3.9° and 20.3°. Both of these angles which have exactly the same commensurate lattice constant of 3.6 nm. The thermal conductivities of the two structures are identical indicating that the functional dependence of the thermal conductivity in the low angle regime continues to be on the lattice constant rather than on the misorientation angle.

As the lattice constant increases, the reciprocal lattice constant decreases, so that Umklapp scattering should become more accessible to the low-energy, small-wavevector phonons that determine the thermal conductivity. All else being equal, the increased scattering should decrease the thermal conductivity. While this picture is consistent with the trends in the large angle regime, in the small angle regime (<13°), this is the opposite of the trend that we observe. However, as the misorientation angle returns to zero degrees, the thermal conductivity must return to that of the AB aligned structure, and this is what we observe. In this talk, we will describe the thermal transport in the low angle regime, and we will present our analysis of the thermal transport that includes the average phonon velocities and density of modes, and we will also present a spectral decomposition of the lattice thermal conductivity determined from the force-velocity cross correlation function.

The investigation uses both nonequilibrium molecular dynamics (NEMD) and ab-initio density functional theory (DFT) combined with the phonon Boltzmann transport equation. For the NEMD direct calculations of the thermal conductivity, the width of the simulated bilayer graphene structures is approximately 10 nm. To ensure that the results do not

References:

QN04.04.23

Our recent calculations show that as the misorientation angle falls below 13.2°, the thermal conductivity initially increases rapidly as the angle decreases from 13.2° to 7.3°, even though the commensurate lattice constant is monotonically increasing. As the angle continues to decrease down to 1.9°, which is the smallest angle simulated, the thermal conductivity gradually returns to its unrotated value.

For small angles with minimal commensurate unit cells, the commensurate lattice constants monotonically increase as the angles decrease, so that it is not clear what determines the functional dependence of the thermal conductivity in the small angle regime. Is it the misorientation angle or the commensurate lattice constant? To answer this question, we investigated two very different angles, 3.9° and 20.3°. Both of these angles which have exactly the same commensurate lattice constant of 3.6 nm. The thermal conductivities of the two structures are identical indicating that the functional dependence of the thermal conductivity in the low angle regime continues to be on the lattice constant rather than on the misorientation angle.

As the lattice constant increases, the reciprocal lattice constant decreases, so that Umklapp scattering should become more accessible to the low-energy, small-wavevector phonons that determine the thermal conductivity. All else being equal, the increased scattering should decrease the thermal conductivity. While this picture is consistent with the trends in the large angle regime, in the small angle regime (<13°), this is the opposite of the trend that we observe. However, as the misorientation angle returns to zero degrees, the thermal conductivity must return to that of the AB aligned structure, and this is what we observe. In this talk, we will describe the thermal transport in the low angle regime, and we will present our analysis of the thermal transport that includes the average phonon velocities and density of modes, and we will also present a spectral decomposition of the lattice thermal conductivity determined from the force-velocity cross correlation function.

The investigation uses both nonequilibrium molecular dynamics (NEMD) and ab-initio density functional theory (DFT) combined with the phonon Boltzmann transport equation. For the NEMD direct calculations of the thermal conductivity, the width of the simulated bilayer graphene structures is approximately 10 nm. To ensure that the results do not
depend on the sample width, multiple increasing widths are simulated until there is no longer any width dependence. The sample lengths are varied from 20 nm to 426 nm. The largest structure contains 317,600 atoms.


Acknowledgement
This work was supported by the National Science Foundation under Award NSF EFRI-1433395. The ab initio simulations used the Extreme Science and Engineering Discovery Environment (XSEDE), supported by National Science Foundation (NSF) grant No. ACI-1548562 and allocation ID TG-DMR130081.

QN04.04.23
Spatial Mapping of Thermal Boundary Conductance at Interfaces of Metal and 2D Materials David B. Brown1, Wenqing Shen2, Diego Vaca3, Xufan Li4, Kai Xiao4, David B. Geohegan5 and Satish Kumar4, Georgia Institute of Technology, Atlanta, Georgia, United States; 6Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Improving the thermal transport across interfaces is a necessary consideration for micro- and nano-electronic devices and necessitates accurate measurement of the thermal boundary conductance (TBC) and understanding of transport mechanisms. Two-dimensional transition metal dichalcogenides (TMDs) have been studied extensively for their electrical properties, including the metal-TMD electrical contact resistance, but the thermal properties of these interfaces are significantly less explored irrespective of their high importance in their electronic devices. We isolate individual islands of MoSe2 grown by chemical vapor deposition using photolithography and correlate the 2D variation of TBC with optical micrograph images of the MoSe2 islands. We measure the 2D spatial variation of the TBC at metal-MoSe2-SiO2 interfaces using a modified time-domain thermoreflectance (TDTR) technique which requires much less time than full TDTR scans. The thermoreflectance signal at a single probe delay time is compared with a correlation curve which enables us to change the signal in real-time with respect to the TBC at metal-MoSe2-SiO2 interface as opposed to recording the decay of the thermoreflectance signal over delay times of several nanoseconds. The results show higher TBC across Ti-MoSe2-SiO2 interface compared to Al-MoSe2-SiO2. An image analysis method is developed to differentiate the TBC for different MoSe2 layers, which reveals the TBC in single-layer regions is higher than bilayer. We perform traditional TDTR measurements over a range of delay times and verify TBC is higher at Ti-MoSe2-SiO2 interface compared to Al-MoSe2-SiO2 highlighting the importance of the choice of material to heat dissipation at electrical contacts in TMD devices.

QN04.04.24
The Influence of Interfacial Structure and Strain Energy on Phonon Transport Riley C. Hans and G. J. Snyder; Northwestern University, Chicago, Illinois, United States.

Phonon transport across interfaces is an inherently complex topic of great scientific and technological importance to fields ranging from microelectronics to energy materials. Here, I will present several experimental and theoretical results which aim to establish a fundamental understanding of heat transfer across interfaces, specifically grain boundaries (GBs). First, I will demonstrate how phonon diffraction and dimensionality crossover effects arise when the nanoscale structure of interfaces and GBs is considered. An expression for the relaxation time of phonon interacting with GB strain fields (τ(GB)) is presented and is shown to effectively describe the temperature dependence of the lattice thermal conductivity (κL) of polycrystals at low temperatures (<100 K). At these temperatures the total phonon relaxation time is dominated by interactions with GBs, and the temperature dependence of κL reveals important information about the nature of the phonon-GB interaction. Next, an experimental study is presented where the thermal boundary resistance is measured on individual Si-Si twist GBs at different twist angle. The thermal boundary resistance at GBs again seems to be dominated by the interfacial strain field. Finally, it is shown how the thermal boundary resistance can be controlled by modifying the GB complexion with 2D materials. Specifically, several layers of graphene can be introduced into the GBs of skutterudite materials which dramatically increases the materials thermal boundary, while negligibly effecting electronic transport. This results in a significant improvement in zT and a 24% improvement in device efficiency which was measured experimentally.

QN04.04.25
Study of Phonon Transport in GaN Thin Films Using Boltzmann Transport Equations Nitish Kumar, Ajit K. Vallabhaneni and Satish Kumar, Georgia Tech, Atlanta, Georgia, United States; 2Qualcomm, San Diego, California, United States.

GaN is a promising wide bandgap material for radio frequency and power electronics applications due to higher breakdown voltage and efficiency. However, the high-power dissipation could result in the formation of hot-spots and high temperature in localized regions which could significantly affect the performance and reliability of these high-power devices. Therefore, it’s necessary to understand the thermal transport mechanism in GaN based electronics to develop efficient thermal solutions. In this study, we develop a phonon transport model based on the first-principles Density Functional Theory (DFT) along with the non-gray Boltzmann Transport Equations (BTE) to predict the steady-state and transient spatial temperature distribution in a GaN thin film with localized power dissipation. First-principles DFT calculations are conducted to calculate the phonon properties of the GaN, such as phonon life time, mean free path and group velocity. The full non-gray BTE is solved across the entire domain to calculate the temperature distribution near the hot spot in the thin film where ballistic effects dominate and the results are compared with the Fourier model. We observed that the BTE model is needed to obtain accurate temperature distribution as the Fourier model would significantly under predict the hot spot temperature. However, solving BTE in the entire domain might be time-consuming and expensive. Therefore, we developed acceleration techniques to reduce computation time of solving the BTEs without significant loss of accuracy in temperature estimation. BTEs for phonon modes with Knudsen number less than the cut-off are simplified into Fourier like equations to improve computation time. These equations are selected based on a cut-off Knudsen number, which can be adjusted to get desired accuracy. The effect of diffusive-ballistic effects on hot spot temperature rise in time has been investigated. The results from this work will help us understand the mechanism of phonon transport in the GaN thin film and provide insights for the future design of GaN based electronic devices.

QN04.04.26

Nanoscale phonon properties have recently received attention because new material properties can be designed by tailoring vibrational behaviour. This has triggered significant efforts towards a better nanoscale control and manipulation of thermal processes in materials. In this context, the reduction of the physical size of materials also resulted in the need of improved spectroscopic techniques and methods to characterize phonon and thermal properties of materials with higher spatial resolution. Recently, aberration-corrected electron microscopes were equipped with monochromators, thus opening the doors for phonon spectroscopy studies in nanomaterials using an electron probe of the size of a hydrogen atom. For instance, this advancement allowed us to obtain spatially-resolved maps of phonon scattering in a single nanoparticle (≤100 nm) with nanometer resolution [1]. Also, due the nature of the inelastically scattered phonons by phonons, the scattering amplitude exhibit a dependence on temperature and the spatial distribution of the scattering has several types of localization. In this work, exploiting the characteristic of the phonon scattering, we present a non-invasive method to measure the local temperature of a single nanostructure using an electron probe. We determined the local temperature of nanostructures with high precision (down to 1K) and sub-nanometer spatial resolution (down to 2Å) [2].

We obtained energy-loss/energy gain spectra from nanostructures (nanostructures and nanoparticles) and using a Nion STEM microscope equipped with a monochromator to study the phonon response in the infrared range using a 1.5 Å probe with an energy spread of 9 meV. Our instrument allows the detection of acoustic bulk phonon excitations down to 20 meV [1]. The amplitudes of the energy-loss and energy-gain probabilities are linked by the Boltzmann factor, as established by the Principle of Detailed Balancing (PDB). We measured the nanostructure temperature by plotting the logarithm of the ratio of the scattering amplitude on the gain and loss sides of zero energy. The obtained curves are linear with a 2 standard deviations and agreed very well with the accepted values for room temperature conditions. Similar results were obtained for measurements at high temperatures (up to 1000 K). We found also that the temperature of the phonon scattering is highly correlated with the temperature of the nanostructure. This result is also consistent with the previously measured temperature gradient in nanostructures with isolated particles [1], suggesting that temperature gradients from the inside towards the surface should be detectable. We also investigated the localization degree of our measurements and we found that highly-localized scattering, associated with the excitation of short-wavelength acoustic phonons, can be used to perform measurements with atomic resolution, because bulk scattering can vary drastically within neighboring atom columns [3]. Meanwhile, surface phonon polaritons can yield accurate averages over a region of interest (several nanometers).
We show that the temperature of a nanofluid can be measured experimentally using phonon scattering, and we verify that PDB holds for nanomaterials at thermal equilibrium. We also think this method holds much promise for studies aimed at understanding nanoscale thermal response (heat transfer, nanoscale energy transport) in nanostructures. We acknowledge support of U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0005132.


QN04.04.27 Prediction of Thermal Conductance at Liquid-Gas Interfaces Using Molecular Dynamics Simulations James Gonzalez, Josue Ortega and Zhi Liang; Mechanical Engineering, California State University, Fresno, Fresno, California, United States.

Using molecular dynamics (MD) simulations and theoretical calculations, we study heat transfer across liquid-gas interfaces within a planar heat pipe. To determine the thermal conductance (Kapitza conductance), G<sub>K</sub>, at the interface, two heat transfer mechanisms, namely, conduction and evaporation/condensation are considered. In the case of interfacial heat conduction, gas molecules, particularly non-condensable gas molecules, exchange heat with liquid surfaces through gas-liquid collisions, and the theoretical expression for G<sub>K</sub> is derived from the kinetic theory of gases. For interfacial heat transfer by evaporation or condensation, the theoretical expression for G<sub>K</sub> is derived from the Schrage relationships. To assess the accuracies of the theoretical expressions for G<sub>K</sub>, we compare these theoretical predictions to the G<sub>K</sub> obtained directly from MD simulations. For all cases studied, the theoretical predictions agree with the MD simulation results very well. If the density of non-condensable gas in the heat pipe is much higher than that of the working fluid in the gas phase, we find that the interfacial heat conduction could contribute significantly to the total heat flux across the liquid-gas interfaces. The effect of G<sub>K</sub> at liquid-gas interfaces on the overall heat transfer efficiency in a planar heat pipe is discussed.

QN04.04.28 Lone-Pair Electrons Do Not Necessarily Lead to Low Lattice Thermal Conductivity—An Exception of Two-Dimensional Penta-CN<sub>2</sub> Huimin Wang¹,², Nanjing University, Nanjing City, China; ¹University of South Carolina, Columbia City, North Carolina, United States.

It has long been documented in literature that, the lone-pair electrons are generally thought to lead to low lattice thermal conductivity (κ<sub>L</sub>) of bulk materials by inducing strong phonon anharmonicity. In this paper, we show an exceptional case of two-dimensional (2D) penta-CN<sub>2</sub>. Based on the comparative study of four 2D systems, namely planar C<sub>2</sub>N and penta-CN<sub>2</sub> possessing lone-pair electrons and their respective lone-pair electrons free counterpart graphene and penta-graphene, we find that the lone-pair electrons do not necessarily lead to low κ<sub>L</sub> of low-dimensional materials. Opposite tendency of lone-pair electrons affected κ<sub>L</sub> are observed. The κ<sub>L</sub> of planar C<sub>2</sub>N (103.02 Wm<sup>-1</sup>K<sup>-1</sup>) is substantially lower than graphene (3094 Wm<sup>-1</sup>K<sup>-1</sup>) due to the well understood strong anharmonicity induced by the lone-pair electrons. However, penta-CN<sub>2</sub> with lone-pair electrons exhibits more than doubled κ<sub>L</sub> (660.71 Wm<sup>-1</sup>K<sup>-1</sup>) than penta-graphene (252.95 Wm<sup>-1</sup>K<sup>-1</sup>), which is unexpected and contradictory to the traditional theory of lone-pair electrons leading to low κ<sub>L</sub>. By analyzing the bond characteristics, electronic structure and the spatial distribution of lone-pair electrons, the underlying mechanism is attributed to the two competing effects of lone-pair electrons on the phonon anharmonicity. The wide spatial extension of the non-symmetrically distributed lone-pair electrons significantly decreases the bond angle by introducing strong repulsion to the bonding electrons. This leads to the homogenization of bond lengths in penta-CN<sub>2</sub> and compensates the strong lattice anharmonicity due to the far retraction of lone-pair electrons from the N nucleus towards the missing link of the tetrahedron composed of C, N atoms and the collective lone-pair electrons. Consequently, the atomic vibration around the equilibrium position tends to be more harmonious and thus the phonon anharmonicity is weakened, leading to much higher κ<sub>L</sub> of penta-CN<sub>2</sub> than that of penta-graphene. This study offers insight into the unprecedented positive effect of lone-pair electrons on κ<sub>L</sub> from the microscopic picture of electronic structure, which deepens our understanding on phonon anharmonicity and could also facilitate material design with targeted thermal conductivity.

QN04.04.29 Thermal Properties of Phase Change Memories at Device Length Scale Kiumars Aryang¹,², John Gaskins¹, David Olson¹ and Patrick Hopkins¹,²; ¹Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia, United States; ²Department of Materials Science and Engineering (courtesy), University of Virginia, Charlottesville, Virginia, United States.

Chalcogenide materials such as Ge<sub>2</sub>Se<sub>3</sub>Te<sub>2</sub> (GST), which upon thermal excitation undergo structural transition between amorphous and crystalline phases with applied thermal load, have emerged as a potential material candidate for new memory technologies due to prospective gains in speed, device lifetime, and capacity. In these devices, thermal transport plays a pivotal role as it dictates the efficiency of the read/write process as well as overall power consumption. Here, we measure thermal properties relevant to device operation at material length scale similar to those used in actual devices, such as thermal conductivity, thermal boundary resistance (TBR), and sound speed of both amorphous and crystalline GST using time-domain thermoreflectance. Based on the acoustic echoes obtained from picosecond acoustic results we measure the sound speed of amorphous and crystalline GST to be approximately 2900 m/s. Moreover, we report the TBR with different spacer compositions (W, SiO<sub>2</sub>, and SiN) in contact with GST. The SiN/GST interface shows the highest TBR compared to both W and SiO<sub>2</sub> interlayers. In the case of all spacer compositions, the crystalline GST interface shows a higher interface resistance compared to its amorphous counterpart. Additionally, very thin layers of tungsten (≤ 4 nm) possess a higher TBR when compared to layers thicker than four nanometers, which we attribute to ballistic transport of phonons.

QN04.04.30 Phonon Coupling in Layered Nanomaterials—A Novel Mechanism to Modulate Thermal Conductivity Abhinav Malhotra, Kartik S. Kothari and Martin Maldovan; Georgia Institute of Technology, Atlanta, Georgia, United States.

Thermal conductivity engineering in semiconductors has been primarily focused on using diffusive scattering of phonons at interfaces to reduce thermal transport. In this talk, we show that a novel mechanism - phonon coupling in layered nanomaterials - can be used to both enhance and reduce thermal transport. By considering Silicon and Germanium based structures (bi-layers and tri-layers), we show that the thermal conductivity of the Silicon layer can be reduced below its free-standing value, without directly manipulating its surface properties. We present a methodology to impact the phonon coupling and quantify the role of structural parameters including layer dimensions and interfacial properties. We also show that the same underlying mechanism of phonon coupling leads to thermal conductivity enhancement of the Germanium layer above its free-standing value. The results of this work expand the rational material design paradigm by creating capabilities beyond the diffusive scattering mechanism and adds to the fundamental understanding of phonon transport at nanoscale.

QN04.04.31 Control of Thermal Conductance Through Overlapping Graphene Sheet Junction Phononics Charles A. Sievers¹, Miguel Munoz Rojo², Eric Pop³ and Davide Donadio¹; ¹University of California Davis, Davis, California, United States; ²Stanford University, Stanford, California, United States.

Low dimensional materials, such as graphene and carbon nanotubes, have the highest thermal conductivity, which makes them a promising substrate for heat dissipation in nanoscale electronics. Interfaces play a crucial role in determining the thermal dissipation performances in microelectronic systems and thermal resistance. While it is now well established that graphene has an extremely high in-plane thermal conductivity, the thermal energy flow at multi-layer graphene junctions, and at the interfaces between graphene layers and bulk substrates remains mostly unresolved. Here we consider a two-to-one layer graphene junction, either suspended or supported on silica, for which experimental measurements reported very low thermal conductance. In quantitative agreement with experiments, molecular dynamics and lattice dynamics calculations show that the thermal conductance is one order of magnitude smaller than that of a suspended single graphene sheet, and it stems from the weak interaction between the layers in the bilayer part of the junction. Thermal conductance is further reduced by 30% upon addition of silica substrate due to interference of graphene flexural modes with the substrate. These modes are the major heat transport mechanism that are unaltered by changes in junction surface area. These results show promising ways in which we can modulate thermal dissipation through layered 2D material junctions.

QN04.04.32 Mass Accommodation at a High-Velocity Water Liquid-Vapor Interface Jihui Nie¹, Anirban Chandra¹, Zhi Liang² and Pawel Keblinski³; ¹Rensselaer Polytechnic Institute, Troy, New York, United States; ²California State University, Fresno, California, United States.
We use molecular dynamics to determine the mass accommodation coefficient (MAC) of water vapor molecules colliding with a rapidly moving liquid-vapor interface. This interface mimics those present in collapsing vapor bubbles and characterized by large interfacial velocities. We find that at room temperature, the MAC is generally close to unity, and even with interfaces moving at 10 km/s, it has a large value of 0.8. Using a simplified atomistic fluid model, we explore the consequences of vapor molecule interfacial collision rules on pressure, temperature, and density of a vapor subjected to an incoming high-velocity liquid-vapor interface.

**QN04.04.33**
Thermal Transport in Semicrystalline Polyethylene by Molecular Dynamics Simulation Jixiong He, Tingyu Lu and Jun Liu; North Carolina State University, Raleigh, North Carolina, United States.

Recent research has highlighted the potential to achieve high-thermal-conductivity polymers by aligning their molecular chains. Combining with other merits, such as low-cost, corrosion resistant, and lightweight, such polymers are attractive for heat transfer applications. Due to their quasi-one-dimensional structural nature, the understanding on the thermal transport in those ultra-drawn semicrystalline polymer fibers or films is still lacking. We build the ideal repeating units of semicrystalline polyethylene and studied their dependence of thermal conductivity on different crystallinity and interlamellar topology using the molecular dynamics simulations. We found that the conventional models, such as the Choy-Young’s model, the series model, and Takayanagi’s model, cannot accurately predict the thermal conductivity of the quasi-one-dimensional semicrystalline polyethylene. A modified Takayanagi’s model was proposed to explain the dependence of thermal conductivity on the bridge number at intermediate and high crystallinity. We also analyzed the heat transfer pathways and demonstrated the substantial role of interlamellar bridges in the thermal transport in the semicrystalline polyethylene. Our work could contribute to the understanding of structure-property relationship in semicrystalline polymers and shed some light to the development of plastic heat sinks and the thermal management in flexible electronics.

**QN04.04.34**
Thermal Conductivity of ALD Grown PbTe/PbSe Superlattice Thin Films Mallory E. DeCoste1,2, Xin Chen1, Kai Zhang3, Helmut Baumgart4 and Patrick Hopkins1; 1University of Virginia, Charlottesville, Virginia, United States; 2Johns Hopkins University Applied Physics Lab, Laurel, Maryland, United States; 3Old Dominion University, Newport News, Virginia, United States.

We report on the thermal properties of lead chalcogenide-based superlattice thin films grown on planar silicon wafers by atomic layer deposition (ALD). The concept of controlling thermal energy carriers in thin film superlattices of PbTe/PbSe by varying the total thickness and period thickness is experimentally investigated in this work. We demonstrate the use of time domain thermoreflectance (TDTR) to measure the cross-plane thermal conductivity of these systems in order to understand the role of size effects and boundary scattering on the thermal conductivity of the PbTe/PbSe superlattices. The thin films of varying compositions resulted in thermal conductivities that are not strongly dependent on the period thickness, and are weakly dependent on the samples total thickness. This suggests that incoherent transport dominates in the thickness regime studied. Additionally, our results show that increased phonon boundary scattering introduced by the periodicity of the superlattice structure is effective for reducing the thermal conductivity.

**QN04.04.35**
Diffusive to Ballistic Heat Flow Transition in GaP Nanowires Daniel Vakulov1, Subash Gireesan1-3, Ruben Chavez2, Milano Y. Swinkels2, Tom Vogelars3, Pol Torres2, Ilaria Zardo2, Marcel van de Ven1; 1Universitat Politècnica de Catalunya, Barcelona, Spain; 2Department of Applied Physics, TU Eindhoven, Eindhoven, Netherlands; 3Department of Physics, Universitat Basel, Basel, Switzerland; 4Department de Fisica, Universitat Autònoma de Barcelona, Barcelona, Spain; 5Center for Computational Energy Research, Eindhoven, Netherlands; 6Kavli Institute of Nanoscience, Delft, Netherlands.

Realizing ballistic transport at room temperature is challenging due to the decrease of phonon mean free paths with increasing temperature. Only a few studies have reported this non-diffusive behavior1.2. Ballistic transport was observed in SiGe nanowires up to lengths of 8.3 μm at room temperature1. This behavior was attributed to the localization of short-wavelength phonons due to alloy scattering, and long-wavelength phonons with a long mean free path dominating the transport. Longer wires showed diffusive transport1. Here, we report room-temperature ballistic transport in thin ultrapure GaP nanowires and an abrupt, temperature-insensitive transition to diffusive behavior on increasing the diameter. Nanowires with diameter ranging from 25-140 nm were grown using the vapor-liquid-solid technique with gold droplets as a catalyst. TEM images revealed that these wire have an atomically flat side facets, with a thin (2 nm) amorphous gallium oxide layer on top. Thermal conductivities of the individual wires were measured using a suspended device membrane1 with Pt meanders on top, which can be used as a heater and a thermometer. For thick wires (diameter ≥ 50nm), the thermal conductance increases linearly with length, indicating diffusive behavior. For thin wires (diameter ≤ 25 nm), the thermal conductance is independent of length, indicating a transition to ballistic phonon transport. The ballistic transport at room temperature continues to the longest nanowires of 14 μm that we could study. The thermal conductance is surprisingly insensitive to a temperature above 50 K. This shows that boundary scattering dominates other scattering mechanisms. The experimental results are interpreted using a model based on Landauer’s formalism for phonon transport3. This model was used to describe heat flow in thin silicon nanowires4 and in holey silicon5. It takes into account boundary scattering and neglects all other scattering mechanisms. Due to the presence of the thin amorphous oxide layer on the surface, the strength of the boundary scattering is determined by the k-vector perpendicular to the axis of the nanowire. The modes with a small perpendicular k-vector scatter weakly and have a high dependence mean free path l(o), while the other modes scatter strongly, having a mean free path of the order of the diameter of the wire d. The model results agree well with heat transport measurements on 25 and 50 nm diameter wires, correctly predicting the magnitude of the thermal conductance and its length dependence. We explain the diffusive to ballistic transition by the localization of phonons in the 25 nm wire that reflects diffusively from the amorphous oxide layer, accompanied by a strong increase in the mean free path of phonons that reflect mostly specularly. Our work demonstrates the possibility of increased heat extraction in nanostructures and opens new avenues for phonon-based devices.

References

**QN04.04.36**
Surface Plasmon Effects on Interfacial Heat Transport Processes in Gold Nanorods Andrew P. Kelliher1, John A. Tomko2, Brian B. Lynch2, Joseph Tracy3 and Patrick Hopkins1; 1University of Virginia, Charlottesville, Virginia, United States; 2North Carolina State University, Raleigh, North Carolina, United States.

Metal nanoparticles are efficient generators of heat via the photothermal effect, in which the surface plasmon resonance is excited by incident light. Surface scattering of excited electrons contributes to the generation of hot electron-hole pairs, which then thermalize and couple with the lattice to generate phonons. Anisotropic nanostructures often exhibit additional surface plasmon modes which can be tuned by altering their geometries. Gold nanorods, studied here, exhibit plasmon resonance in the near-infrared, making them suitable for applications in medical technologies, such as drug delivery or photothermal cancer therapy. This additional plasmon resonance can be tuned further during the synthesis process to allow of soft robotics components using shape memory polymers. Furthermore, silica overcoatings having various morphologies have been developed to improve thermal stability of these nanorods up to 873 K while reducing toxicity. When using gold nanorods for photothermal applications, the primary descriptors of thermal transport are electron-phonon coupling in the gold nanorods and at their interfaces, and the phonon-phonon thermal boundary conductance across the nanorod/matrix interface. Using complementary ultrafast pump-probe laser techniques, we explore the effect of the surface plasmon on these two thermal descriptors of gold nanorods in a polymer matrix. By using variable pump wavelengths, we are able to selectively excite the surface plasmon modes. We elucidate the effect of the plasmon excitation on electron-electron coupling and electron-phonon coupling, while showing that it has little effect on phonon-phonon thermal boundary conductance at times after the electrons have equilibrated with the phonons. Additionally, in order to assess the effects of overcoatings on thermal boundary conductance, we compare results for three types of overcoated nanorods: those with full silica shells, those with silica/iron oxide composite shells, and those with silica/iron oxide composite shells.
Comprehensive Modeling of Electron and Thermal Transport in Thermionic Energy Conversion Systems
Devon Jensen, Mohammad Ghahami and Keunhan Park;
University of Utah, Salt Lake City, Utah, United States.

Over recent years, thermionic energy conversion (TEC) has received keen revived attention for direct heat-to-electric power generation [1–3]. However, large electrode work functions and the accumulation of negative space charge between electrodes are major issues that have restricted the use of TEC to high-temperature heat sources exceeding 1500K. As one of the potential approaches to mitigate these issues, previous works have proposed to have a sub-micron vacuum gap between the electrodes [4-6]. However, their theoretical models are not comprehensive in accurately modeling the size effect on the electron and thermal transport processes across sub-micron gap distances.

The present work provides a comprehensive look at electron and thermal transport in a TEC system as the gap separation is scaled from tenths of a millimeter down to tens of nanometers. To this end, the energy barrier profile between the electrodes, \(W(x)\), is calculated within the electrostatic framework by considering space and image charge effects. The thermionic current density and heat transfer rate are then calculated by applying the determined maximum value of the energy barrier, \(W_0\), to the rigorous charge transport model. In addition, quantum tunneling of electrons is also considered for nanoscale gap distances. Near-field radiative heat transfer is an important thermal transport mechanism to be considered when the inter-electrode gap distance becomes comparable to or smaller than the thermal wavelength [7]. The summation of the electron (thermionic and electron tunneling) and radiative heat fluxes between the electrodes allows for an energy balance calculation to provide a more realistic anode temperature for device operation and thermionic energy conversion efficiency.

Moreover, we theoretically demonstrate that the nanoscale gap distance shifts a portion of the field-induced charge acceleration regime from a negative to positive operational voltage range, resulting in the enhancement of thermionic power generation by tailoring the surface roughness of the cathode electrode. The obtained results will ultimately provide insight into the design and thermodynamic performance analysis of nano-gap TEC systems based on a fundamental understanding of nanoscale charge and thermal transport physics.


QN04.04.38 Lithium Intercalation-Induced Thermal Conductivity Change of Amorphous WO\(_3\) Films
Ryuta Kobayashi,1 Tong Shen,2 Ayano Nakamura,3 Shunro Harada1,3, Miho Tagawa1,2 and Toru Ujihara1,3,4; 1Department of Materials Process Engineering, Nagoya University, Nagoya, Japan; 2Department of Materials Science and Engineering, Nagoya University, Nagoya, Japan; 3Center for Integrated Research of Future Electronics, Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan; 4GaN Advanced Device Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology, Nagoya University, Nagoya, Japan.

Thermal switch, which can turn on/off the heat flow, plays an important role in thermal management. Ion intercalation materials have attracted interests because of their ability to change the thermal conductivities with electrochemical reactions. In our previous study, we have reported a drastic and reversible change in the thermal conductivity of amorphous WO\(_3\) film with H intercalation (0.2 W/mK \(\rightarrow\) 3.1 W/mK). This phenomenon is exactly the function of a thermal switch. In this study, we try to demonstrate another thermal conductivity change of amorphous WO\(_3\) by Li intercalation and investigate the mechanism of the thermal conductivity change from a viewpoint of local cluster network model. Amorphous WO\(_3\) film was prepared on ITO coated glass substrate at room temperature by RF magnetron sputtering in Ar-O\(_2\) atmosphere. Li intercalation into the WO\(_3\) film was performed with 1.0 M LiClO\(_4\) in propylene carbonate. The structure change of the film was determined by X-ray diffraction and Raman spectroscopy. The thermal conductivity of the film was measured by ac calorimetric method.

With increasing intercalated Li concentration, the thermal conductivity decreases, then remarkably increased at around x \(=\) 0.20, and subsequently decreases again. This tendency is similar to amorphous WO\(_3\)-H system. Peak positions of Raman spectra in amorphous WO\(_3\) almost to the same as those of crystalline WO\(_3\) except for the existence of peak of W=O double bonds in the spectra of amorphous WO\(_3\). It seems that cluster of atoms forms network. As the Li content increases, the Raman spectrum becomes more broad, indicating that the structure become disordered. Thus, heat transfer is inhibited by the disorder of the structure. On the other hand, a drastic increase in thermal conductivity may result from local structural phase change. In crystalline WO\(_3\) film, as the Li content increases, the crystal structure of Li\(_2\)WO\(_3\) transforms from monoclinic to tetragonal and further to cubic structure. The thermal conductivity of the cubic structure is larger than those of the other phases. Raman spectrum of amorphous WO\(_3\), at the Li content around the grain boundary. The exhaustive explanation of thermal transport properties in superionic Ag\(_2\)Te in our study will support the future design of superionic conductors based thermoelectrics and more broad energy systems composed of ordered-disordered materials.

QN04.04.39 Molecular Dynamics Study of Thermal Transport in Ordered-Disordered Superionic Ag\(_2\)Te and Its Traditionally Contradictory Enhancement by Nanotwin Boundary
Biao Wu1, Yuangang Zhou2 and Ming Hu1; 1RWTH Aachen University, Aachen, Germany; 2University of California Los Angeles, Los Angeles, California, United States; 1University of South Carolina, Columbia, South Carolina, United States.

Superionic Ag\(_2\)Te, like other superionic conductors, has its unique characteristic of the coexistence of ordered anion lattice and disordered liquid-like motion of cations and has a great potential in thermoelectric applications. Yet physical mechanisms of thermal transport in such ordered-disordered systems have not been well understood, and the traditional lattice vibration concept, i.e., phonons are regarded as heat carriers, fails to explain the governing mechanism in such structures. In our study, we calculate the thermal conductivities and their contributing factors of superionic Ag\(_2\)Te based on the heat flux linear response theory using equilibrium molecular dynamics simulations and explore thermal transport mechanisms by focusing on the effects of the boundary and the nanotwin effect. By decomposing the overall thermal conductivity into two contributing components we found that the convective thermal conductivity is dominant in superionic Ag\(_2\)Te, which results from the free movement of Ag ions. As a consequence, the total thermal conductivity increases abnormally with temperature due to the enhanced cations' mobility at elevated temperatures. Meanwhile, the nanotwin boundary, which has been utilized as a phonon scatter, has been found in our study to unexpectedly improve thermal transport in superionic Ag\(_2\)Te due to the strengthened movement of Ag ions around the grain boundary. The exhaustive explanation of thermal transport properties in superionic Ag\(_2\)Te in our study will support the future design of superionic conductors based thermoelectrics and more broad energy systems composed of ordered-disordered materials.

QN04.04.40 Giant Reduction of Thermal Transport in Polyvinylidene Fluoride Under Tensile Strains
Tengfei Ma, Lei Cao and Yan Wang; Department of Mechanical Engineering, University of Nevada, Reno, Reno, Nevada, United States.

Polyvinylidene fluoride (PVDF), a non-reactive thermoplastic polymer, exhibits overwhelming prospect on pyroelectric and electrocaloric applications. Generally speaking, PVDF is usually polymerized as α-phase but its β-phase isomeride received higher attention due to the significant pyroelectric properties. In this work, we conducted first-principle calculations to investigate thermal transport properties of β-phase PVDF. The thermal conductivities of single-chain and bulk crystalline PVDF were calculated under different tensile strain. The obtained thermal conductivity of bulk PVDF is several orders of magnitude larger than experimental data due to the perfectly aligned chains in our simulation. We found that giant reduction of thermal conductivity in single PVDF chain can be induced by applied strain. The phonon dispersion relations show that this phenomenon might be caused by the reduced group velocity in stretched PVDF chains. The result is contrary to previous observations on amorphous polymers in which thermal conductivities rise with increased strain due to better alignment of chains in stretched amorphous polymers. Therefore, we can conclude that thermal transport in stretched PVDF is mainly coupled by two mechanisms: one is the reduced contribution to the thermal conductivity by each chain and the other is the enhanced contribution by the aligning of chains.

QN04.04.41 AFM Cantilever Based Near Field Radiation Heat Transfer Measurement
Ramteja Kondakindi, Jui-Yung Chang and Liping Wang; Arizona State University, Tempe, Arizona, United States.
It is predicted that when two surfaces are placed in close proximity such that the distance between them is less than the thermal wavelength, radiative heat flux could be significantly enhanced for being the blackbody limit due to near-field radiation or photon tunnelling through nanometer scale vacuum gaps. Recently experimental demonstrations of super-Planckian near-field thermal radiation have been reported between plate-plate or tip-surface configurations. This study aims to develop a home-built thermal metrology for measuring near-field radiative heat transfer between a sphere and a planar surface with well controlled gap distances down to a few nanometers. A bi-material atomic force microscope (AFM) cantilever is used as a thermal sensor, whose temperatures will be measured simultaneously by two means: difference signal due to bending and sum signal with thermorelectance obtained from a position sensitive diode (PSD). Careful calibrations for both bi-material cantilever bending and thermorelectance will be carried out first to establish the relation between the tip temperature and the PSD difference signal from bending, or the sum signal from thermorelectance. The temperature of AFM cantilever will be varied by the laser power, while a power meter will be used to measure the incident, reflected and scattered laser beams to determine absorbed laser power. When the planar sample maintained at room temperature is brought closer with a piezo stage at sub-nm resolution, it is expected that the AFM cantilever will be cooled due to enhanced near-field radiative heat transfer. The thermal conductance from the near-field thermal radiation at different gap distances will be calculated from measured cantilever temperature, absorbed laser power, and sample temperature. Silica microsphere will be attached to the AFM cantilever to promote the near-field radiative heat transfer. Reference samples like quartz and silicon wafers will be measured first to compare with reported experimental results and theoretical calculations for validation. Near-field measurement results with SiC wafer, 2D materials like graphene, or nanostructured metamaterials will be reported. The outcomes of this research aim to enhance the fundamental understandings of radiative heat transfer in the near-field which could lead to advances in microelectronics, optical data storage and thermal systems including energy conversion devices.

QN04.04.42
Evaporation Rates for Molecular Fluids—Molecular Dynamics and Schrage Relationships
Anirban Chandra1, Zhi Liang2 and Pawel Keblinski3; 1Rensselaer Polytechnic Institute, Troy, New York, United States; 2California State University, Fresno, Fresno, California, United States.

Using molecular dynamics (MD) simulations we study the steady state evaporation and condensation processes of molecular polar fluids in a one-dimensional heat-pipe geometry. The non-equilibrium mass flow is driven by controlling the temperatures of the source/sink. The resulting mass fluxes as a function of driving force are evaluated for systems with pure working fluids (e.g., water) and in the presence of non-condensing gases (e.g., water + air). Our results indicate that the molecular velocity distributions in the vapor phase are indeed Maxwellian distributions shifted by the velocity of the macroscopic vapor flow, as assumed in Schrage’s theoretical analysis. Furthermore, we evaluate the mass accommodation coefficient as a function of temperature using equilibrium simulations. Consequently, we determine that the Schrage equations describe the evaporation-condensation rates of molecular fluids with moderate accuracy.

SESSION QN04.05: Hydrodynamics and Disorder
Session Chairs: Patrick Hopkins and Barry Zink
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 124 A

8:00 AM QN04.05.01
Emergence of Hydrodynamic Phenomena in Collective and Kinetic Regimes
E. Xavier Alvarez1, Javier Bafaluy1, Juan Camacho1, Xavier Cartoixà2, Pol Torres1, Albert Beardo Rico1 and Lluc Sendra1; 1Physics, Universitat Autonoma de Barcelona, Bellaterra, Spain; 2Electrical Engineering, Universitat Autonoma de Barcelona, Bellaterra, Spain.

Two main characteristics make nanoscale thermal transport in semiconductors a complex phenomena full of nuances. The first is the importance of momentum conservation in the phonon-phonon collisions (Normal scattering)1-3. This kind of scattering is not able to destroy momentum and consequently in their presence the phonon distribution cannot relax to its equilibrium form. The second is the large scale range that span the phonon mean free path spectrum4. Because of this the connectivity between two regions in a sample (non-locality) depends on the kind of phonons connecting these regions. The consequence is that heat transport at the nanoscale is still an incompletely described topic.

Phonon hydrodynamics has emerged in the last years as a candidate to cover this gap. The appearance of this regime has been associated to the dominance of non-collisions. Its presence has been proven in 2D materials or at low temperatures5-6, when N-collisions are dominant and in consequence collective effects can be observed easily. But recent works have shown that hydrodynamic effects can still have an important impact when resistive collisions are dominant7-9. In this case its presence has to be noticed through indirect evidences. Hydrodynamics has been used, for example, to understand the lack of validity of the Mathiessen rule in silicon or the dependence of the Thermal Boundary Resistance between two materials on the size of the contact.

Kinetic Collective Model (KCM) has been developed to describe heat transport using two key concepts. On one side, the splitting in collective regime (when normal scattering is dominant) and kinetic regime (when it is not important). On the other side, the inclusion of nonlocal and memory effects that introduce hydrodynamic behavior in the description. From the combination of both concepts it can be shown that hydrodynamic phenomena can emerge in both, collective and kinetic regimes, with different particularities in each case.

The equations obtained from the model are simple enough to be solved using finite element computational tools. We will show the results from a recent developed module implemented in COMSOL. Using KCM equations in combination with ab initio calculated parameters we will describe hydrodynamic effects in 2D materials like graphene and in conventional semiconductors like silicon an use the results to interpret some of the most relevant experimental observations of the last years.


8:30 AM QN04.05.02
Role of Normal Scattering for Thermal Resistance in Phonon Hydrodynamics
Xun Li and Sanghee Lee; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Hydrodynamic phonon transport occurs when normal scattering (N-scattering) is much stronger than umklapp scattering. Due to its momentum-conserving nature, N-scattering does not directly cause thermal resistance. In particular, when a sample is extremely large and thus diffuse boundary scattering can be ignored, N-scattering alone cannot cause any thermal resistance. For a sample with finite size, however, N-scattering combined with diffuse boundary scattering affects thermal resistance. We discuss two different mechanisms of thermal resistance associated with N-scattering in finite-sized samples when phonon transport is in the strong hydrodynamic regime. The discussion is based on the Monte Carlo solution of the Peierls-Boltzmann transport equation in both real and reciprocal spaces using an ab initio three-phonon scattering matrix. First, when a sample has a finite width but an infinite length along the heat flow direction, the thermal resistance occurs due to the momentum transfer along the lateral direction (i.e., perpendicular to heat flow direction), called phonon viscous damping effect. The stronger N-scattering, the slower the momentum transfer, resulting in lower thermal resistance. Second, when a sample is infinitely wide but has finite length along the heat flow direction, phonons emitted from heat reservoirs change their distributions from static to displaced Bose-Einstein distributions upon N-scattering. During this transition between non-collective and collective phonon flows, N-scattering causes thermal resistance. The thermal resistance of this case depends on the shape of phonon dispersion provided that the sample length is larger than the mean free path of N-scattering. For graphitic materials, the transition between collective and non-collective phonon flows reduces heat flux by 50% from the ballistic case at room temperature.
Hydrodynamic Transport and Thermal Energy Dissipation

In an overwhelmingly large group of conducting materials thermal and electrical transport are directly related via the Wiedemann-Franz law, which states that the product of the thermal conductivity and the electrical resistivity divided by the temperature is a constant, yielding the Sommerfeld value. In stark contrast to these ordinary conductors, heat and charge flow can de-couple in strongly correlated materials yielding thermal energy dissipation and transport behavior that can be described by the theory of hydrodynamics. In this talk, we will present recent thermal and magneto-electric transport experiments on heat and charge flow in the Weyl semimetal tungsten di-phosphide [1]. We observe a strong violation of the Wiedemann-Franz law that coincides with a transition from a conventional metallic state at high temperatures to a hydrodynamic electron fluid below 20 K. The hydrodynamic regime is characterized by a viscosity-induced dependence of electrical resistivity on the sample width and magnetic field. Based on the accompanying decoupling of momentum conserving and relaxing scattering processes we illustrate that both thermal and electrical transport are bound by the quantum indeterminacy applied to energy dissipation, independent of the underlying transport regime.

[1] thermal and electrical signatures of a hydrodynamic electron fluid in tungsten diphenphide

In-Plane Heat and Charge Transport in sub-100 nm Thin Films—Surprises from Nanotubes to Magnetic Alloys

Theoretical understanding of phonon dynamics in nanostructures with a significant degree of surface disorder is far from complete. Here, we show how concepts from chaos theory, such as the level-spacing distribution and the geometric mean free path, can shed light on the universal features in phonon dynamics and thermal transport across structures of different dimensions and roughness. Within this context, we simulate lattice dynamics using Monte Carlo in the semiclassical limit and the finite-difference time-domain (FDTD) solution to the elastic wave equation for the elastic-solid limit.

Prominent Localization of Phonons and Strong Deviation to Matthiessen's Scattering Rule Introduced by Dislocation Engineering Heat Transport in Nanoparticle-in-Alloy Composites—The Role of Mie Scattering

Dislocations have prominent scattering to phonons. Tuning dislocation patterns is an effective method to control the thermal conductivity in thermoelectric materials. However, clear impact of dislocation on phonon scattering is still missing, although substantial efforts have been devoted to this issue. By performing non-equilibrium molecular dynamics (NEMD) simulation, the thermal transportation of a rock salt structure PbTe crystal and a body-centered cubic (bcc) iron crystal containing quantitative dislocations have been studied. For the first time, temperature distribution in proximity to the dislocation, spectral heat flux and frequency dependent phonon mean free paths (MFPs) are explicitly obtained. The results not only show that quantitative dislocations suppress the lattice thermal conductivity but also reveal detailed phonon-dislocation scattering processes, which is due to the localization of phonon modes in sample with dislocations. Moreover, we provide a way to scale the scattering rate between the phonons and dislocations which may offer a guidance for engineering to regulate the lattice thermal conductivity by introducing or removing dislocations.

In this talk, we will present recent thermal and magneto-electric transport experiments on heat and charge flow in the Weyl semimetal tungsten di-phosphide [1]. We observe a strong violation of the Wiedemann-Franz law that coincides with a transition from a conventional metallic state at high temperatures to a hydrodynamic electron fluid below 20 K. The hydrodynamic regime is characterized by a viscosity-induced dependence of electrical resistivity on the sample width and magnetic field. Based on the accompanying decoupling of momentum conserving and relaxing scattering processes we illustrate that both thermal and electrical transport are bound by the quantum indeterminacy applied to energy dissipation, independent of the underlying transport regime.

[1] Thermal and electrical signatures of a hydrodynamic electron fluid in tungsten diphenphide

J Gooth, F Menges, N Kumar, V Stiβ, C Shekhar, Y Sun, U Drechsler, B Gotsmann

Nature Communications 9, 4093, 2018

Phonon Dynamics in Disordered Nanostructures—A Chaos Perspective

Irena Knezevic; University of Wisconsin-Madison, Madison, Wisconsin, United States.

Joseph P. Feser; University of Delaware, Newark, Delaware, United States.

Prominent Localization of Phonons and Strong Deviation to Matthiessen's Scattering Rule Introduced by Dislocation

Ben Xu; Tsinghua University, Beijing, China.

SESSION QN04.06: Nanostructures and Interfaces II

Session Chairs: F. Xavier Alvarez and Irena Knezevic

Wednesday Morning, April 24, 2019

PCC North, 100 Level, Room 124 A

In-Plane Heat and Charge Transport in sub-100 nm Thin Films—Surprises from Nanotubes to Magnetic Alloys

Barry Zink; University of Denver, Denver, Colorado, United States.

Recent advances in thermoelectric materials through nanoscale engineering bring both tremendous promise and serious fundamental measurement challenges. For materials ranging from graphene to carbon nanotube hybrids to nanomagnetic systems or films, samples with one or more dimensions on the sub-100 nm scale are always difficult to thermally characterize. Our approach to these measurements uses micro- and nanomachined thermal isolation platforms that allow exceptional control over thermal gradients and unambiguous alignment of this gradient in the plane of a thin film or nanoscale sample. Micromachined electrical leads enable thermal conductivity, electrical conductivity, and Seebeck effect measurements all on the exact same sample. This allows particularly powerful probe of both the Wiedemann-Franz law and the thermoelectric figure-of-merit, ZT.

In this talk, I will first focus on our recent work on increasing ZT in sub-100 nm thin films by reducing thermal conductivity, which we have demonstrated in two very different systems. In the first, disordered films formed from carefully-selected semiconducting single-wall carbon nanotubes (CNT) show dramatic reduction in thermal conductivity when doped with organic acids.[1] This reduction is likely driven by increased phonon scattering caused by the proximity of the CNT and the dopant molecule, and raises ZT for both n- and p-type films to some of the largest values yet observed in organic systems.[2] More surprising is a strong non-monotonic temperature dependence of thermal conductivity seen in certain preparations of CNT films that drives a sharp increase in ZT over a narrow temperature range.[3] It is not yet clear if this effect is driven by changes in phonon populations or scattering, and further study could lead to a new route to reducing thermal conductivity in CNT thermoelectric systems. The second system showing a surprising reduction in thermal conductivity and increase in ZT are evaporated films of gold. Across a wide range of film thickness we see very strong violations of the Wiedemann-Franz law in gold films, with a measured Lorenz number reduced to less than half the free-electron values near room temperature.[4] Finally I will discuss magnetic alloy films where careful examination of the Wiedemann-Franz law indicates a large additional thermal conductivity. Ongoing work will clarify if this is driven by primarily by phonons or magnons in these systems, and point toward new ways to manipulate spin degrees of freedom in ferromagnets with heat. Work at DU is supported by the NSF (DMR-1709646) and DOE-CINT (DE-AC04-94AL85000).

4) Mason, et al., "Violation of Wiedemann-Franz Law through reduction of thermal conductivity in gold thin films," in preparation

11:00 AM QN04.06.02
Unexpected High Inelastic Phonon Transport Across Solid-Solid Interface—Modal Nonequilibrium Molecular Dynamics Simulations and Landauer Analysis Tianli Feng, Yang Zhang, Jingli Shi and Xiulin Ruan; Purdue University, West Lafayette, Tennessee, United States.

As a crucial part in thermal management, interfacial thermal transport is still not well understood. In this paper, we employ the newly developed modal nonequilibrium molecular dynamics to study the Si/Ge interfacial thermal transport and clarify several long-standing issues. We find that the few atomic layers at the interface are dominated by interfacial modes, which act as a bridge that connects the bulk Si and Ge modes. Such bridging effect boosts the inelastic transport to contribute more than 50% to the total thermal conductance even at room temperature. The apparent inelastic transport can even allow effective four-phonon processes across the interface when the mass difference between the two materials is large. Surprisingly, optical phonon modes can contribute equal or more thermal conductance than the acoustic modes due to the bridging effect. From the modal temperature analysis, we find that the phonon modes are in strong modal nonequilibrium near the interface, which impedes the thermal transport. The widely used Landauer approach that does not consider the phonon nonequilibrium can lead to inaccurate results. We have modified the Landauer approach to include the inelastic transmission and modal thermal nonequilibrium. The approach is used to analyze our modal NEMD results, and the mode-dependent phonon transmission function that includes inelastic scattering has been derived. Our results unveil the fundamental thermal transport physics across interfaces and will shed light on the future engineering in thermal management. It provides a method of calculating modal phonon transmission functions that includes inelastic scattering from molecular dynamics.

11:15 AM QN04.06.03
Interfacial Scattering in Boltzmann Transport Simulations of Phonons Giuseppe Romano1, Aria Hosseini1, Jackson Harter1, Todd Palmer1 and Alex Greaney1; 1University of California, Riverside, Riverside, California, United States; 2Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3School of Nuclear Science and Engineering, Oregon State University, Corvallis, Oregon, United States.

Packages that efficiently simulate the Boltzmann transport of phonons have become an established research tool for predicting thermal transport in micro and nanoscale dielectric devices. However, the widespread application of these tools, particularly in industry, is currently hindered by the numerical difficulty of modeling the thermal processes at boundaries and interfaces where the thermal state of the two materials is large. Surprisingly, optical phonon modes can contribute equal or more thermal conductance than the acoustic modes due to the bridging effect. From the modal temperature analysis, we find that the phonon modes are in strong modal nonequilibrium near the interface, which impedes the thermal transport. The widely used Landauer approach that does not consider the phonon nonequilibrium can lead to inaccurate results. We have modified the Landauer approach to include the inelastic transmission and modal thermal nonequilibrium. The approach is used to analyze our modal NEMD results, and the mode-dependent phonon transmission function that includes inelastic scattering has been derived. Our results unveil the fundamental thermal transport physics across interfaces and will shed light on the future engineering in thermal management. It provides a method of calculating modal phonon transmission functions that includes inelastic scattering from molecular dynamics.

11:30 AM *QN04.06.04
Ultrafast Electron-Phonon and Plasmon Scattering Effects in Metals, Non-Metals and Interfaces Probed with Tunable Wavelength Sub-Picosecond Pulses Patrick Hopkins; University of Virginia, Charlottesville, Virginia, United States.

We report on a series of experimental measurements designed to understand the role of hot excited electrons and plasmons and resulting electron-phonon coupling on nonequilibrium electron thermal transport in metals, non-metals and metal/non-metal interfaces. We implement a pump-probe thermoreflectance using sub-picosecond laser pulses with wavelength tunability through the visible and into the IR. We use this tunable photon energy to demonstrate that electron-phonon coupling in metals (e.g., Au, Al, Pt) and non-metals (e.g., silicon and GaAs) can be strongly energy dependent, and when probing near interband transitions, scattering rates can be strongly dictated by electron number densities. We then consider the role of electron-phonon coupling at interfaces between gold and an insulating non-metal substrate with an adhesion layer between the gold and the substrate. We show that under conditions of electron-phonon nonequilibrium and ballistic electron transport, the thermal conductance due to electron-phonon coupling can lead to enhancements in the overall thermal boundary conductance across metal/non-metal interfaces. Next, we consider the heat transport processes across metal/doped semiconductor interfaces, where the energy barrier at the metal/non-metal interface is low enough to promote electron injection across this boundary. We show that electron injection across this boundary can be used as a means to control the electronic thermal transport and electron-phonon scattering rates in semiconductors within the electronic Kapitza length near the metal/doped semiconductor interface. Finally, we study the role that plasmon excitation can have on these electron interfacial properties by considering metal/doped CdO interface in which the CdO supports near-IR plasmon modes.

SESSION QN04.07: Topology and Phonon Transport
Session Chairs: George Fytas and Austin Minnich
Wednesday Afternoon, April 24, 2019
PCC North, 100 Level, Room 124 A

1:30 PM *QN04.07.01
Chiral Phonons in Two-Dimensional Materials Life Zhang; Nanjing Normal University, Nanjing, China.

The theoretical finding on chiral phonons at Brillouin-zone corners (valleys) of two-dimensional honeycomb lattices has attracted wide attention in the study of phonon chirality very recently [1]. In this talk, firstly I will report and the experimental verification of chiral phonons in monolayer tungsten diselenide [2], where the chiral phonons are identified by the intervalley transfer of holes through hole-phonon interactions during the indirect infrared absorption, and their chirality are confirmed by the infrared circular dichroism arising from pseudoangular momentum conservation. Then I report our recent findings on chiral phonons in center-stacked bilayer triangle lattices where the phonon chirality remain robust with changing sublattice mass ratio and interlayer coupling [3], graphene/hexagonal boron nitride heterostructure where broken inversion symmetry and the interlayer interaction of G/h-BN not only open the phononic gaps but also lift the degeneracy of left-handed and right-handed chiral phonons at valleys [4], and in 2+3 × 3+3 honeycomb superlattices where the nondegenerate chiral phonons at valleys are folded phonon Brillouin-zone center thus being more measurable by helicity-resolved Raman scattering [5]. Collectively, our results on the chiral phonons in these two-dimensional materials could stimulate more experimental and theoretical studies on chiral phonons and promote the future applications on the phonon-chirality-based phononics.

Reference:

2:00 PM QN04.07.02
Symmetry-Driven Phonon Chirality and Transport in 1D Materials Lucas Lindsay, Tribhuvan Pandey, Carlos Polanco, Valentino Cooper and David Parker; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Symmetry and dimensionality are essential factors defining lattice dynamics and thermal conductivity in materials. Here, we will present physical insights developed from predictive first principles Peierls-Boltzmann transport in 1D chains and compare them with 2D and bulk materials. In particular, we will discuss how symmetry gives rise to phonon chirality in 1D chains from which phonon-phonon scattering rules are derived. These symmetry-based selection rules limit thermal resistance, while chain coupling breaks these in weakly bonded bulk systems, giving lower κ and larger κ anisotropy.
2:15 PM QN04.07.03
Topological Origins of the Inverse Dependence of the Thermal Conductivity on Temperature of Crystalline and Non-Crystalline Solid States Above Approximately 50 K
Caroline S. Gorham and David E. Laughlin; Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Thermal transport properties of the solid state are intimately tied to the structure that forms from the undercooled atomic liquid. Above approximately 50 K, the thermal conductivity of glasses ubiquitously decreases with decreasing temperatures while the thermal conductivity of crystalline materials rises sharply with decreasing temperatures; the origin of this inverse behavior has remained a matter of inquiry over the past century. This work elucidates the topological origins of the thermal transport properties of the solid state, by adopting a quaternion number to characterize the orientational order that develops by atomic clustering at temperatures below the melting temperature.

Solidification of undercooled liquids towards crystalline ground states may be viewed as a higher-dimensional realization of Bose-Einstein condensation of superfluids, that are characterized by a complex orientational order parameter, such as helium superfluids and superconductors. Just as complex ordered systems are considered to exist in restricted dimensions in two- and one-dimensions, quaternion ordered systems in four- and three-dimensions may be considered to exist in restricted dimensions. In restricted dimensions, misorientational fluctuations in the form of spontaneously generated topological defects prevent conventional long-range order at finite temperatures. Third homotopy group topological point defects in quaternion ordered systems play the role of vortices in complex ordered systems.

In restricted dimensions, one may observe either a phase-coherent or a phase-incoherent low-temperature state by changing the non-thermal tuning parameter that characterizes the ordered system. For example, in two- and one-dimensional charged complex ordered systems (i.e., Josephson junction arrays), superinsulating ground states may be realized with infinite electrical resistance that is a mirror image of superconductivity. Similarly, solidification in four- and three-dimensions (i.e., quaternion ordered systems) can result in either crystalline and non-crystalline low-temperature states. Resulting thermal transport properties of orientationally-ordered (crystalline) and orientationally-disordered (non-crystalline) solid states are inverse to one another above approximately 50 K, in analogue to the electrical transport properties of Josephson junction arrays across the superconductor-to-superinsulator transition.

2:30 PM Break

3:30 PM QN04.08.01
Exploring the Upper Limits of Thermal Conductivity in Molecular Crystals
Austin J. Minnich; California Institute of Technology, Pasadena, California, United States.

Molecular crystals that conduct heat are of interest both fundamentally and for applications. Long-standing questions regarding the thermal transport properties of these materials include how crystals with complex unit cells can still possess high uniaxial thermal conductivity despite their large scattering phase space, and what is the distribution of phonon mean free paths in actual molecular crystals that possess many defects. Here, we address these questions using advances in numerical and experimental tools. First, we use ab-initio calculations to show that high thermal conductivity along the chain axis arises from phonon focusing despite intense phonon scattering in the complex crystal. Second, we report the observation of ballistic phonons on micron length scales in semi-crystalline polyethylene using transient grating spectroscopy, allowing us to determine the mean free path distribution. These works elucidate the microscopic details of heat transport in molecular crystals.

4:00 PM QN04.08.02
Phonon Lifetimes in the Molecular Crystal α-RDX
Gaurav Kumar, Francis VanGessel and Peter W. Chung; Mechanical Engineering, University of Maryland, College Park, Maryland, United States.

Molecular crystals form an important class of materials. They appear in vital medical and defense applications ranging from pharmaceuticals to energetics. Thermal and vibrational properties are particularly critical to know due to their influence over, for instance, tabling strength and initiation sensitivity. The accurate prediction of certain phonon properties like the thermal conductivity and energy transfer rate requires knowledge of anharmonic vibrational properties, in particular the phonon lifetimes. In this study we extend techniques previously used for atomic crystals to predict phonon lifetimes for all branches of the molecular crystal α-RDX. We use two different techniques to predict phonon lifetimes - anharmonic lattice dynamics (ALD) [1] [2] and frequency domain normal mode decomposition (NMD) [3]. We for the first time present the temperature and frequency dependence of phonon lifetimes due to normal and Umklapp processes in α-RDX, and identify phonon modes with high scattering rates which result in high energy transfer rates. Our results indicate that phonon lifetimes in α-RDX do not have a monotonic relationship with frequency. In fact, some high frequency phonons are found to exhibit longer lifetimes than low frequency phonons. This is in contrast with trends observed in atomic crystals [3] [4] [5] and predictions based on Callaway’s model [6] where higher frequency phonons generally have a smaller lifetime and therefore participate more in diffusive transport mechanisms. The longer lifetimes of optical modes enable these modes to carry a significant proportion of phonon thermal energy. In fact, in contrast to the marginal role optical phonons play in thermal transport in atomic crystals, optical phonons in the molecular crystal α-RDX contribute 63-78% of the total thermal conductivity.

References

4:15 PM QN04.08.03
Chain Rotation Significantly Reduces Thermal Conductivity of Single-Chain Polymers
Hao Ma and Zhirong Tian; Cornell University, Ithaca, New York, United States.

Kevlar (polyparaphenylene terephthalamide) and PBDT (poly(2,29-disulfonyl-1,49-benzidine terephthalamide))-derivatives have very similar chemical structures with aromatic rings. In this study, thermal conductivities of their single chains were calculated using molecular dynamics simulations. Chain rotation was found to be the key to reducing thermal conductivity. By introducing a new chain rotation factor (CRF), we can easily quantify the chain rotation level of single-chain polymers. We demonstrated that thermal conductivity decreases as the CRF increases. We performed further calculations on phonon properties and unveiled that the small thermal conductivity led by large chain rotation can be attributed to reduced phonon group velocities and shortened phonon mean free paths. Insights obtained in this study can be used for tuning the thermal conductivity of various polymers and facilitating their various applications including thermal energy conversion and management.

4:30 PM QN04.08.04
Recent Applications of Brillouin Light Scattering Spectroscopy to the Study of Thermomechanical Properties of Nanostructured Soft Materials
Zuyuan

Acknowledgements: This work was supported by the U. S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.
Nanostructured materials hold promises for a wide range of applications. For example, they could be used as drug delivery carriers, novel coating ingredients, and interfacial fillers. The realization of these applications, however, relies on a good understanding of the thermomechanical properties (e.g., glass transition temperature, elasticity) of the nanomaterials, which could deviate from those of their bulk counterparts due to effects like an increased surface-to-volume ratio and spatial confinement. As a non-contact, non-destructive technique, Brillouin light scattering (BLS) spectroscopy provides unique characterizations of the thermomechanical properties of nanostructured materials via the resolution of hypersonic phonons. In this contribution, three recent applications of BLS will be presented. First, BLS is employed to study core-shell polymer based colloids. The observed nanoparticle vibrational modes provide a direct probe of the particle surface mobility, revealing the critical role of the shell architecture on the glass transition temperature and elasticity of the nanoparticles. Second, BLS is applied to “disentangle” the role of chain conformation (e.g., grafting density, degree of polymerization) on the mechanical properties of thin films of polymer tethered particle (particle-brush) materials with different grafting density and chain length. The bulk modulus, determined based on the BLS-detected sound velocities and the Bragg peak intensity, shows a maximum in intermediate to low grafting density systems, where the hard (silica) cores are partially exposed due to the conformational fluctuations of the grafted (polyethylene) polymer chains. Third, BLS is utilized to understand the effect of confined polymer layers on the effective mechanical properties of hybrid materials composed of alternating polystyrene and hectorite nanolayers. The clear resolution of the direction-dependent quasi-longitudinal, quasi-transverse, and pure-transverse phonon modes from BLS leads to the determination of the full elastic tensor of the materials by assuming them to be transversely isotropic; materials with thinner PVP layers (i.e., stronger confinement) exhibit higher Young’s modulus in the directions parallel and perpendicular to the layers. These studies demonstrate BLS as an effective tool for studying the thermomechanical properties of nanostructured materials. The results improve our understanding of the structure-property relation in the three material systems, and contribute to realizing their applications through guided engineering.

Development of ultrafast electron and X-ray scattering methods has enabled direct routes to probing atomic-scale structural dynamics in myriad chemical and materials systems [1,2]. This in turn has led to new physical insights into molecular and crystal-lattice responses associated with chemical-bond dynamics, phase transformations, electron-lattice correlations, and nanoscale structural motion. Importantly, the detailed nature of materials responses are likely influenced by ever-present lattice discontinuities and nanoscale morphological features. Thus, direct probing of the local structural dynamics would provide a richer, more detailed picture of the overall evolution of ultrafast energy deposition and transport. Here, I will discuss how fs electron imaging with an ultrafast electron microscope (UEM) [3] can be used to directly visualize specific coherent, low-frequency acoustic-phonon dynamics in a variety of materials, with particular emphasis placed on resolving the influence of lattice discontinuities. After a brief overview of the instrumentation and the general experimental approach, I will describe how the concepts of static, real-space imaging with conventional electron microscopes can be used to visualize local coherent lattice oscillations in crystalline materials. Once described, these concepts will aid in understanding a number of photoinduced phonon behaviors we have observed in transition metal dichalcogenides (TMDs) and thin crystals of archetypal semiconductors [4-7]. For example, in TMDs (WSe$_2$, MoS$_2$, and TaS$_2$) we have found that fs photoexcitation leads to the generation of coherent phonon wavetrains preferentially at vacuum-crystal interfaces and extended crystal step edges. This arises via an initial impulsive expansion along the c-axis of van der Waals stacking direction occurring within the first few picoseconds after ultrafast excitation. This impulsive interlayer expansion induces the launch of coherent interlayer phonon wavetrains due to the picosecond development of a phase mismatch between the neighboring layers owing to varying total transit times of the speed-of-sound c-axis phonons between the outer layers. As with the stacking direction, the coherent interlayer modes propagate at the speed of sound (e.g., 5 mm/ps) and initially along a single wavevector oriented perpendicular to the defect nucleation sites prior to the first scattering events. Similarly, in strongly-photoexcited thin crystals of undoped Ge, we directly image a variety of spatially and temporally heterogeneous effects; including the launch of highly-coherent phonon wavetrains propagating with high phase velocities (observable up to 35 mm/ps with the UEM modalities employed), the significantly-delayed (i.e., 10s of picoseconds more) generation of phonon wavetrains relative to the precise moment of fs photoexcitation, and time-varying phase-velocity dispersions displaying single-exponential relaxation to the Ge bulk speed of sound (5 mm/ps) within one nanosecond following fs photoexcitation. This survey of recent results will serve to illustrate the rich and detailed information obtainable with fs electron imaging, with particular emphasis placed on the low-frequency modes highlighted here.

Reference:

9:00 AM QN04.09.02
Temperature-Dependent Thermal Diffuse Scattering Measurements Using Scanning Transmission Electron Microscopy
Geoffrey Wehmeyer,$^{1, 2}$ Karen C. Busillo$^{1}$, Andrew Minor$^{1, 4, 5}$ and Chris Dames$^{1, 4}$
$^{1}$Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States; $^{2}$Mechanical Engineering, Rice University, Houston, Texas, United States; $^{3}$National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; $^{4}$Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; $^{5}$Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Scanning transmission electron microscopy (STEM) thermometry techniques open new possibilities for mapping temperature (T) with high spatial resolution. Existing STEM thermometry methods based on measuring thermally-induced strains must content with small thermal expansion coefficients (~10 parts per million (ppm)/K) for some materials, as well as potentially non-local relationships between strain and temperature. In contrast, the well-known mechanism of thermal diffuse scattering (TDS) offers promise for inherently local T measurements, and Debye-Waller theory predicts that many materials should display large temperature coefficients (~1000 ppm/K) at room temperature and above. This T-dependent TDS has not been leveraged for STEM thermometry, however, because the Debye-Waller effect on the Bragg peak intensity is overwhelmly by the effects of thermal tilts and thermal drift. Here, we demonstrate quantitative TDS measurements using STEM by measuring the diffuse background intensity (rather than the Bragg peak intensity) in energy-filtered scanning electron nanodiffraction patterns. Applying virtual apertures to these diffraction patterns during post-processing allows us to quantify the T-dependent TDS in the diffuse background. Within one nanosecond following fs photoexcitation, this diffuse signal, we measure a position-averaged temperature coefficient of 2400 ± 400 ppm/K for a single-crystal gold film averaged between T=100 K and T=300 K, and compare our results with the predictions of Debye-Waller theory. The measurements display typical temperature uncertainties of 8 K and temperature sensitivities of 51 K Hz$^{-1}$. This TDS-based STEM thermometry demonstration provides a step towards the goal of non-contact nanoscale temperature mapping of thin nanostructures or microelectronics.

9:15 AM QN04.09.03
Nanoflake Thermal Transport Through Silicon Nanoengineered Metalattices Probed Using Coherent EUV Beams
Begona Abad Mayor$^{1}$, Joshua Knobloch$^{1}$, Travis D. Frazer$^{1}$, Jorge Nicolas Hernandez Charpak$^{1}$, Hui Yan Cheng$^{1, 3}$, Alex Grede$^{1, 3}$, Andrew Glaid$^{1, 3}$, Noel Gibelink$^{1, 3}$, Tom Mailoak$^{1, 3, 4}$, Prathish Mahale$^{1, 6}$, Weinan Chen$^{1, 6}$, Yihuang Xiong$^{1, 6}$, Ismaela Dabo$^{1, 6}$, Vincent Crespi$^{3, 4}$, Disha Talreja$^{1}$, Venkat Gopalan$^{2, 3, 6}$, John Badding$^{3, 4}$, Henry Kaptay$^{1}$ and Margaret Murnane$^{1}$
$^{1}$JILA - CU Boulder, Boulder, Colorado, United States; $^{2}$Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania, United States; $^{3}$Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States; $^{4}$Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; $^{5}$Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, United States; $^{6}$Materials Science and Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

In this contribution, three recent applications of BLS will be presented. First, BLS is employed to study core-shell polymer based colloids. The observed nanoparticle vibrational modes provide a direct probe of the particle surface mobility, revealing the critical role of the shell architecture on the glass transition temperature and elasticity of the nanoparticles. Second, BLS is applied to “disentangle” the role of chain conformation (e.g., grafting density, degree of polymerization) on the mechanical properties of thin films of polymer tethered particle (particle-brush) materials with different grafting density and chain length. The bulk modulus, determined based on the BLS-detected sound velocities and the Bragg peak intensity, shows a maximum in intermediate to low grafting density systems, where the hard (silica) cores are partially exposed due to the conformational fluctuations of the grafted (polyethylene) polymer chains. Third, BLS is utilized to understand the effect of confined polymer layers on the effective mechanical properties of hybrid materials composed of alternating polystyrene and hectorite nanolayers. The clear resolution of the direction-dependent quasi-longitudinal, quasi-transverse, and pure-transverse phonon modes from BLS leads to the determination of the full elastic tensor of the materials by assuming them to be transversely isotropic; materials with thinner PVP layers (i.e., stronger confinement) exhibit higher Young’s modulus in the directions parallel and perpendicular to the layers. These studies demonstrate BLS as an effective tool for studying the thermomechanical properties of nanostructured materials. The results improve our understanding of the structure-property relation in the three material systems, and contribute to realizing their applications through guided engineering.
Nanoscale phononic metamaterials make it possible to engineer the thermal, magnetic, and electronic properties of materials, which is essential for nanoelectronics, thermoelectric and data storage devices, or nanoparticle-mediated thermal therapies [1]. Specifically, nanoscale metalattices are a powerful bottom-up approach to tune the propagation of high frequency phonons - highly ordered nanoscale opal templates allow for precise control over nanoscale structure in which different materials can be infiltrated. Moreover, these metamaterials can be organized into hierarchical structures on length scales from nanometers to micrometers which enable unique properties that cannot be accessed using bulk/layered materials [2,3]. In the case of nanoscale thermal transport, metalattices are a powerful approach to further advance our understanding, which is critical since macroscopic diffusive models completely break down at dimensions that are comparable to the mean free path of the heat carriers [4,5]. However, characterizing energy flow in these metalattices is extremely challenging. Most current techniques rely on visible light, which is limited in wavelength to probing heat flow away from nanostructures >100s of nanometers. We can overcome this limitation by utilizing coherent extreme ultraviolet (EUV) light generated by tabletop high harmonic generation (HHG) [6]. The short pulse duration (~10fs) and wavelength (~30nm) of tabletop HHG sources are an excellent match for probing the intrinsic length- and time-scales relevant to nanoscopic dynamics. In this unique EUV nanotomography technique, we use an ultrafast 800nm femtosecond laser to impulsively heat periodic arrays of nickel nanolines deposited on top of a silicon metalattice. We then probe the cooling of the nanolines, and the resulting thermal transport properties of the metalattice, by monitoring the thermally-induced surface deformation using coherent EUV light. In this work, we show how the thermal transport in silicon metalattices is modified due to the metalattice structure. First, we observe a slow thermal decay of the nanolines through the metalattice, suggesting very low thermal conductivity of the metalattice. Further analysis indicates that, not only do these metalattices have lower thermal conductivity than expected from macroscopic predictions, but that the heat flow is a function of the geometry of the heat sources. In addition, these findings are supported by equilibrium Green–Kubo atomistic simulations which show that silicon metalattices are capable of significantly reducing the thermal conductivity below the prediction of continuum models. This suggests that nanostructured metalattices may be able to impede heat flow even more than had been initially thought. The ability to impede the flow of phonons, while allowing electrical current to flow, can dramatically impact applications such as optimized thermoelectric materials, as well as providing routes for enhanced functionality of other nanodevices.


The vibrational thermal conductivity of solid materials is determined by anharmonic effects, i.e., by features of the potential-energy surface (PES) that are not captured by a harmonic second-order Taylor expansion. However, only the leading contribution to anharmonicity (the third-order term in the Taylor expansion of the PES) is accounted for in typical, perturbative first-principles calculations of thermal conductivities [1]. Higher-order terms are neglected in these models, in spite of the fact that such strong anharmonic effects are known to play a decisive role in many technologically relevant materials, e.g., perovskites [2].

In this work, we discuss the ab initio Green-Kubo method [3], which we have developed for the computation of thermal conductivities in strongly anharmonic materials, and present applications of this method for material-science questions. In this formalism, the full PES is explored via equilibrium ab initio molecular dynamics (AIMD), so to account for all anharmonic effects. The thermal conductivity is evaluated via the Green-Kubo equations [4] using a unique first-principles definition of the heat flux [3]. By this means, incoherent and strongly anharmonic effects are directly treated within the real-space AIMD. Coherent, almost harmonic processes are mapped into a reciprocal-space representation [5], so to overcome finite time and size effects. This robust, asymptotically exact extrapolation scheme allows to obtain accurate bulk thermal conductivities – both for strongly anharmonic materials and for very harmonic materials. This is demonstrated for various representative examples with increasing degree of complexity and anharmonicity (e.g. Si, GaO2, ZrO2, and perovskites). These investigations reveal that a correct treatment of higher-order anharmonicity plays a minor role in good thermal conductors, but is essential to achieve quantitative predictions and qualitative insights in highly anharmonic systems [6]. Eventually, we critically discuss strategies to apply the
developed formalism in a computationally efficient fashion in high-throughput frameworks, e.g., to search for strongly anharmonic materials with ultra-low thermal conductivities.


11:00 AM QN04.10.02
Selective Breakdown of Phonon Quasiparticles Across Superionic Transition in CuCrSe and AgCrSe
Olivier Delaire\(^1\), Jennifer Niedziela\(^1\), Dipanshu Bansal\(^1\), Andrew May\(^2\), Jinxuan Ding\(^3\), Tyson Lanigan-Atkins\(^4\), Georg Ehlers\(^5\), Doug Abernathy\(^6\) and Ayman Said\(^7\); \(^1\) Duke University, Durham, North Carolina, United States; \(^2\) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; \(^3\) Argonne National Laboratory, Argonne, Illinois, United States. Superionic crystals exhibit ionic mobilities comparable to liquids while maintaining a periodic crystalline lattice. The atomic dynamics leading to large ionic mobility have long been debated. A central question is whether phonon quasiparticles—which conduct heat in regular solids—survive in the superionic state, where a large fraction of the system exhibits liquid-like behavior. Here we present the results of energy- and momentum-resolved scattering studies combined with first-principles calculations and show that in the superionic phase of CuCrSe and AgCrSe, long-wavelength acoustic phonons capable of heat conduction remain largely intact, whereas specific phonon quasiparticles dominated by the Cu or Ag ions break down as a result of anharmonicity and disorder. The weak bonding and large anharmonicity of the Cu / Ag sublattice are present already in the normal ordered state, resulting in low thermal conductivity even in the normal phase, at temperatures below the superionic transition. Further, we find a strong repulsion between Cu / Ag neighbors, affecting the diffusion mechanism. These results show how anharmonic phonon dynamics are at the origin of low thermal conductivity and superionicity in this class of materials. Our studies of atomic dynamics and diffusion will help rationalize the emergence of ultralow thermal conductivity for thermoelectrics and facilitate the design of high-performance solid-state electrolytes for next-generation batteries.


11:15 AM QN04.10.03
New Thermal Transport Regime for Partial-Strain-Crystalline Partial-Liquid Materials
Ming Hu; University of South Carolina, Columbia, South Carolina, United States. Materials in partial-crystalline partial-liquid (PCPL) state are now widely used as thermoelectrics [Cu₃Se; PRL 118, 145901 (2017), PNAS 111, 15031 (2014), Nature Mater. 11, 422 (2012)] and battery electrodes [LiS; Nano Energy 18, 89 (2015)], due to their low thermal conductivity and high ionic conductivity, respectively. However, the well-developed computational methods for pure crystalline materials such as anharmonic lattice dynamics coupled with Boltzmann transport equation cannot be straightforwardly used to study such systems. By performing first-principles and molecular dynamics simulations, for the first time we give a robust and detailed explanation of the thermal transport mechanism in PCPL material LiS. At the temperature range in which the system can be regarded as a solid, the large hopping of Li is found to be responsible for phonon thermal conductivity’s deviation from the traditional 1/T relationship. At the high temperature range, the contribution of convection and liquid-phonon interaction increase significantly due to the fluidization of Li ions. Furthermore, there is an interplay between the enhanced phonon scattering and the increased force hopping between neighboring atoms as temperature arises, which results in a dip in the evolution of the virial term around 1200K. When the temperature is higher than 1200 K, the virial thermal conductivity increases with temperature due to the contribution of vibrations with extremely short mean free path (i.e., diffusons). This point is validated by the evolution of the accumulative thermal conductivity with mean free path at 1300 K, more than 40% of the heat carried by the S sublattice is contributed by the carriers with mean free path smaller than a few angstroms, which is the typical hopping distance. Our study provides a clear physical map of the heat transport in phase change materials and describes the key mechanisms to guide the design of the future thermoelectrical materials and battery electrodes.

11:30 AM QN04.10.04
Influence of Ferroelectric Phase Transition on Thermal Properties of GeTe
Diordic Dangic\(^1\), Olle Hellman\(^1\), Eamonn Murray\(^2\), Stephen Fahy\(^3\) and Ivana Savić\(^4\); \(^1\) Tyndall National Institute, Cork, Ireland; \(^2\) California Institute of Technology, Pasadena, California, United States; \(^3\) University College Cork, Cork, Ireland; \(^4\) Imperial College London, London, United Kingdom. GeTe is a well-known thermoelectric material with low lattice thermal conductivity which undergoes a ferroelectric phase transition around 700 K. Using standard first principles calculations, we have shown how the lattice thermal conductivity of PbGeTe alloys could be further suppressed by driving them closer to the phase transition with varying chemical composition \([1,2]\). Here we investigate how this phase transition affects the thermal expansion and the lattice thermal conductivity of GeTe using recently developed first principles methods that account for higher-than-third order anharmonicity \([2,3]\). We find that GeTe exhibits negative thermal expansion near the phase transition \([2]\). This is caused by strong acoustic-soft optical mode coupling \([2]\), which is also responsible for the low lattice thermal conductivity of PbGeTe alloys \([1]\). Surprisingly, our calculations in the framework of temperature dependent effective potentials \([3]\) show an anomalous increase of the lattice thermal conductivity of GeTe at the phase transition. We elucidate the connection between the unexpected conductivity increase and strong anharmonicity.


11:45 AM QN04.10.05
Temperature and Strain Dependent Thermal Conductivity in Ferroelectric Nb:SnTiO Thin Films
Alexandros Sarantopoulos\(^1\), Dipanjana Saha\(^2\), Weeliat Ong\(^3\), Jonathan A. Malen\(^4\) and Francisco Rivadulla\(^5\); \(^1\) Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; \(^2\) Physics, Universidad Santiago de Compostela, Santiago de Compostela, Spain.

SrTiO\(_3\), a well-studied incipient ferroelectric material, has been shown to become ferroelectric in certain conditions of strain and temperature, but the effect on its thermal conductivity is unknown. We present measurements of thermal conductivity in Nb doped SrTiO\(_3\) thin films from 80 K to 300 K. Thermal measurements are conducted using Frequency Domain Thermoreflectance on films deposited via Pulsed Laser Deposition on LSAT, STO, and DyScO\(_3\) substrates, which impose 0.95 % compressive strain, no strain, and 1.15% tensile strain, respectively. We measure a large difference in thermal conductivity between the three substrate imposed strains, where compressive strain results in a 3-fold enhancement to thermal conductivity relative to tensile strain at room temperature. We also observe a greater than 60% reduction in thermal conductivity of the tensioned film as we reduce temperature and it becomes fully ferroelectric. Piezoresponsive Force Microscopy measurements are conducted to investigate the role of ferroelectric domain boundaries as a mechanism for the reduction in thermal conductivity in the ferroelectric phase, where ferroelectric domain boundaries serve as scattering sites for phonon transport. These results are critical to memristor and microwave applications that demand ferroelectric materials, because thermal effects play a major role in performance.

SESSION QN04.11: New Simulation Methods
Session Chairs: Keivan Esfarian and Masahiro Nomura
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 124 A
Over the last decade, a new method has been developed that allows for the detailed study of phonon transport in crystalline solids using first principles methods, such as density functional theory. This approach is powerful, because not only does it exhibit excellent agreement with experiments consistently, it is also capable of predicting the properties of new materials and also explaining anomalous behaviors in some materials. This approach, which is usually based on an expression derived using Fermi’s Golden Rule, however, rather implicitly relies on application of what is often termed the phonon gas model (PGM). The PGM is valid and accurate for pure crystalline solids, which do in fact make up a wide range of the materials of interest for applications. However, there is a growing body of evidence that shows that when one deviates far from an idealized perfect crystal e.g., by introducing randomly distributed defects, alloying elements, interstitials or an interface, the PGM often fails. This is because the shape/character of phonons changes when symmetry is broken and as a result, alloys, amorphous materials and interfaces remain a difficult challenge to describe with the accuracy and predictive capability of first principles.

It is in this respect that molecular dynamics (MD) can play an important role, as it in theory has the ability to fill this gap, since it can be rather ubiquitously applied to any class of solid or molecule with full inclusion of anharmonicity, provided that an accurate empirical potential exists to describe the interatomic interactions. Over the last decade several new methods have been developed that allow for direct calculation of the contributions to thermal conductivity and thermal interface conductance, but the key issue that has been challenging to overcome is still the development of accurate empirical potentials to describe the interatomic interactions. This talk will review recent progress that has been made on this issue, and will outline a potential procedure for how one can utilize first principles calculations to inform empirical potentials that are both fast and accurate (i.e., less than 5% error in forces) consistently for virtually any material where phonons are present. The key is to exploit the fact that phonons are only well defined when all of the atoms vibrate about an equilibrium site i.e., there is no diffusion of atoms or chemical reactions occurring during the MD simulation. Treating this as an implicit constraint, it is possible to use a functional form that accurately reproduces the interactions described by first principles calculations, yet is much faster than machine learned potentials. This talk will provide an overview of this approach and will show initial results for example materials – illustrating for the first time an empirical potential that exhibits less than 5% error in forces, less than 5% errors in dispersion and thermal conductivity, yet can also be used to run stable MD simulations with speed faster than commonly employed potentials such as the Tersoff potential.

2:00 PM QN04.11.02
First Principles Calculations of Thermal Transports in Solids and Liquids Marcello Puligheddu1 and Giulia Galli2, 3; Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, United States; 1Chemistry, The University of Chicago, Chicago, Illinois, United States; 2Material Science Division, Argonne National Laboratory, Argonne, Illinois, United States.

The prediction of the thermal properties of solids and liquids is central to numerous problems in condensed matter physics and materials science, including the study of thermal management of optoelectronic and energy conversion devices. We present two related methods to compute the thermal conductivity of solids and liquids based on ab initio molecular dynamics (MD) at non-equilibrium conditions. Both methods only require calculations of first principles trajectories and atomic forces. We discuss ab initio MD results and computational requirements for solid MgO and liquid water. We compare with experiments and results obtained with classical potentials and, in the case of solids, with results of equilibrium MD simulations and the Boltzmann transport equation [3].


2:15 PM QN04.11.03

Understanding and controlling heat flow on the nanoscale, and through interfaces, is important for applications related to electronics, heat management and thermoelectrics. From a theoretical perspective, the traditional heat flow in Fourier’s law are widely-believed to fail when treating thermal transport on short time- and length-scales. There exists, however, a variety of beyond-Fourier approaches that accurately and rigorously describe nanoscale heat transport, including (among others) the atomistic Green’s function (AGF) method, molecular dynamics (MD), and the Boltzmann transport equation (BTE). Each method has its advantages, from how MD naturally captures anharmonic processes to how the AGF method can provide detailed mode-resolved transmission coefficients, and thus each has proven useful to study and identify important processes and physics.

Over the past few years, we have been working to develop and apply an alternative approach to phonon transport inspired from the lessons of electron transport, referred to as the McKelvey-Shockley (McK-S) flux method. In this talk, I will briefly introduce the McK-S flux method and focus on recent findings from the application of this method to nanoscale and interfacial phonon transport. In particular, the role of ballistic, non-equilibrium, and inelastic scattering effects, which are captured with McK-S, will be discussed. Moreover, I will show how this framework easily handles first-principles phonon dispersions and scattering rates. Owing to its relatively simple form, which promotes physical insights and efficient solutions, and its ability to seamlessly span from the nanoscale to the macroscale, we believe the McK-S method helps complement the existing suite of techniques.

2:30 PM QN04.11.04
Ab Initio Thermal Transport—From Phonon’s Lifetime to Thermal Conductivity Aleksandr V. Chernatynskiy; Missouri University of Science and Technology, Rolla, Missouri, United States.

Ab initio calculations of the thermal conductivity have become routine due to the availability of the several community codes that employ Boltzmann Transport Equation for phonons. An attractive feature of this method is that it gives access not only to the overall thermal conductivity but also to the specifics of the scattering processes for every phonon in the system. Thus, an incredible level of details is emerging which permits to test analytical theories, predict and explain thermal transport properties in a variety of situations or model systems with the additional phonon scattering mechanisms. In this presentation we will review the particulars of the methodology involved, will illustrate its power on the examples of technologically important materials and discuss the applicability of this technique at the limits of high temperature and pressure. To this end, we will consider thermal transport in natural superlattices, Ruddlesden-Popper phases of the SrTiO3 system, phonon lifetimes of the individual phonons in GaAs, and thermal transport in MgO, one of the main constituents of the Earth’s mantle. Results of the simulations will be compared to experiment, where available.

3:00 PM BREAK

SESSION QN04.12: Phononics
Session Chairs: Aleksandr Chernatynskiy and Asegun Henry
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 124 A

3:30 PM QN04.12.01
Directional Heat Flux in Phononic Crystals Masahiro Nomura and Roman Anufriev; The University of Tokyo, Tokyo, Japan.

We experimentally demonstrate formation of directional fluxes of ballistic phonons in one- and two-dimensional silicon phononic nanostructures, in which periodic arrays of nano-
holes or corrugations formed directionality of the thermal phonons. This effect makes guiding and even focusing of heat fluxes possible in silicon nanostructures.

First, using micro time-domain thermoreflectance experiments and Monte Carlo simulations, we studied heat conduction in silicon thin films with aligned and staggered periodic arrays of holes. We found that a significant difference in thermal conductivity appears when the characteristic size of the structures becomes smaller than 100 nm and when the temperatures was decreased [1]. This difference was attributed to directional ballistic phonon fluxes that are formed by the aligned lattice of holes.

Next, we performed in nanowires and experiments with phononic compositions in the corrugated nanowires, though the directionality is weaker [2]. Our analysis shows that the directionality depends on the width of the narrow passages and becomes stronger as the passage narrows [1]. Thus, such periodic phononic structures can be used to guide and emit ballistic phonons in solids. To demonstrate this, we coupled the emission from a two-dimensional phononic crystal into one-dimensional nanowires, in which the ballistic path of the phonons was continued in the direction parallel to the wire. Thus, we measured corresponding nanowire length and temperature dependencies [1].

Finally, we used this concept to create thermal lens nanostructures, which can focus thermal energy in the focal point. Our theoretical and experimental results suggest that the created hotspot is smaller than 200 nm in diameter, and thus can be used in biomedicine, thermoelectrics and wherever selective heating is required [1]. The efficiency of this approach is limited only by the scale and quality of the structures. Thus, as the advancements in nanofabrication technology enable further scaling down, complete control over directionality of ballistic heat fluxes in nanostructures becomes real in the near future.


4:00 PM QN04.12.02

Suppression of Propagon Heat Transport in Amorphous Silicon Nitride Phononic Crystals Naoki Tambo1, Chun Zhou2, Elizabeth M. Ashley2, Yuxuan Liao2, Kouhei Takahashi1, Naito Yasuuki1, Junichiro Shiom1 and Paul F. Nealey3; 1Technology Innovation Division, Panasonic Corporation, Seika-cho, Japan; 2Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, United States; 3Department of Mechanical Engineering, The University of Tokyo, Bunkyo, Japan.

Recent progress in phonon engineering has revealed the effectiveness of nanotechnology on controlling the thermal transport properties of crystalline materials. However, the impact of nanostructuring on amorphous materials has not been examined thoroughly so far. This is surprising given that amorphous materials play a significant role as crystalline materials in various electronic devices. Understanding the thermal transport mechanism of amorphous materials and elucidating the impact of nanostructuring would be highly essential for the management of future electronic devices.

Here, we have studied the impact of ultrafine nanostructuring on the thermal transport properties of amorphous SiN membranes. Samples examined here are SiN, phononic crystals (PnCs) with two-dimensional array of through-holes created at various pitch sizes ranging from 38-1600 nm. Electron beam lithography was used to fabricate SiN PnCs at pitch sizes above 60 nm. On the other hand, directed self-assembly lithography was used to fabricate ultrafine 38 nm-pitch PnCs. Room temperature thermal conductivity \(k\) of the SiN, PnCs were measured by a time-domain thermal reflectance method. We found that \(k\) of SiN strongly depends on the minimum feature size and the surface-to-volume (S/V) ratio of the PnC structure. PnCs at typical pitch sizes of 100-1600 nm whose minimum feature size exceeds 30 nm exhibited \(k > 2.0 \text{ W/mK}\), which was comparable to that of the unpatterned membranes (\(k = 2.5 \text{ W/mK}\)). On the other hand, a significant reduction in \(k\) was observed when the minimum feature size of the PnCs decreased below 30 nm. In these ultrafine PnCs, we found that the reduction in \(k\) is associated with increase in the S/V ratio. This is consistent with the feature reported in crystalline PnCs where diffuse boundary scattering of phonons is enhanced for those that exhibit higher S/V ratios. Recent studies have implied that heat transport in amorphous materials is governed by two types of vibrational modes, i.e., (i) low-frequency propagating modes that increase with relatively long mean free path (MFP) and (ii) high-frequency diffusive mode that decrease with extremely short MFP. The S/V ratio dependence of \(k\) observed here indicates that reduction in \(k\) of the present PnCs is related to enhanced boundary scattering of these propagating modes. Interestingly, we also found that increase in S/V ratio over 0.1 nm\(^{-1}\) does not lead to reduction in \(k\) of SiN, below 1.1 W/mK. This implies that contribution of propagon to heat transport has been suppressed thoroughly by our ultrafine PnC structure, leaving only the diffusions to contribute to heat transport. The present study on amorphous SiN, PnCs demonstrate the effectiveness of multi-scale phonon engineering on material heat transport properties, where we control the high-frequency vibrational modes by the amorphous disorder while that of the low-frequency vibrational modes is controlled by intentional nanostructuring.

4:15 PM QN04.12.03

Thermal Conduction in Titanium Oxide with an Ordered Arrangement of Planar Faults in Nanoscale Shunta Harada1,2, Naoki Kosaka1, Takashi Yagi1, Katsusi Tanaka1, Haruyuki Inui1, Mihoko Tagawa1 and Toru Ujihara1,2; 1Nagoya University, Nagoya, Japan; 2JST PRESTO, Kawaguchi, Japan; 3National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; 4Kobe University, Kobe, Japan; 5Kyoto University, Kyoto, Japan.

Homologous series of the Magnel phase titanium oxides (Ti\(_{2}\)O\(_{n-1}\)) are reduced phases of rutile-type TiO\(_{2}\) and are so-called crystallographic shear structures, in which dense planar faults are periodically introduced in the mother rutile structure with their spacing depending on the oxygen deficiency. Due to the low thermal conductivity owing to dense planar defects and tunability of their structures, the Magnel phases received great attention to the application of thermoelectric materials. Recently, suppression and control of thermal conduction by a phononic crystal with periodic nanostructure fabricated by lithography, in which the interference of low-frequency phonons occurs, was demonstrated. Similar to the phononic crystal, it is considered that the periodic atomic scaled structure in the Magnel phase suppresses the thermal conduction of high-frequency phonons, which would lead to the heat manipulation at room temperature. In the present study we investigated the structural perfection of an ordered arrangement of planar defects as well as the thermal conduction in the Magnel phase titanium oxide.

The crystal of the Magnel phase titanium oxide were prepared by the reduction annealing of rutile-type TiO\(_{2}\) in vacuo. We observed the (132)\(_{\text{hkl}}\) planar faults were periodically introduced with an interval of 2.9 nm in the prepared crystal. The perfection of the periodic arrangement of the planar faults are very high and the periodicity disorder was evaluated to be as small as 0.036 nm by scanning transmission electron microscopy observation in atomic scale. Furthermore, the structure perfection of the planar faults was also high, and the effect of the planar faults were evaluated to be 0.035 nm. From the specularity parameter calculation using these evaluated values, the periodic arrangement of the planar faults is expected to behave as specular interface for phonons up to 16 THz. Time-dominant thermoreflectance (TDTR) measurements revealed that thermal conductivity is decreased by the introduction of the periodic arrangements of the planar faults. Compared to the rutile-type TiO\(_{2}\), the temperature dependence of the thermal conductivity for the Magnel phase titanium oxide was small. The analysis of the temperature dependences of thermal conductivity by the Debye-Callaway model indicates that the increase of Umklapp scattering is caused by the introduction of the periodic planar faults. The Considering the structural perfection of the periodic arrangement of the planar faults, the fold of the Brillouin zone would result in the increase in the Umklapp scattering.

4:30 PM QN04.12.04

Thermal Transport in Amorphous Phononic Crystals Yuxuan Liao1, Naoki Tambo2, Kouhei Takahashi2 and Junichiro Shiom1; 1The University of Tokyo, Tokyo, Japan; 2Technology Innovation Division, Panasonic Corporation, Kyoto, Japan.

Heat in crystalline phononic crystals (c-PnCs) are carried by lattice vibrations (phonons). It is well known that thermal conductivity \(k\) of c-PnCs can be reduced when the length scales of phononic structures are smaller than phonon mean free paths (the size effect), therefore, c-PnCs have been seen as an effective way to tune \(k\) of crystalline materials [1]. Here, we theoretically show that amorphous phononic crystals (a-PnCs) also play an important role for tuning \(k\) for amorphous materials. Indeed, a large proportion of the heat carriers (atormistic vibration modes) in amorphous solids are diffusons, which are expected to have very short effective mean free paths that comparable to interatomic spacings and therefore can be hardly influenced by the size effect [2]. However, there still exist long-wave-length or low-frequency heat carriers (propagons), which propagate at the speed of sound, can have effective mean free paths exceeding tens of nanometers, and thus contribute to significant proportion exceed the total \(k\), especially their tiny density of states [3]. Therefore, it should be possible to tune \(k\) by scattering propagons with phononic structures. To validate the above reasoning, we firstly prepared several a-PnCs samples for amorphous silicon, silicon and silicon nitride, which are 70 nm thick 2D thin films with periodic cylindrical holes of different diameters. Then, the effective mean free paths of propagons and diffusions are obtained by combining Allen-Feldman theory and normal-mode decomposition method [3,4]. Boundary scattering effects for propagons and diffusions are evaluated by Monte Carlo Raytracing method [5]. The results show that \(k\) of these a-PnCs can be as low as ~0.3 W/m K when the neck sizes between the holes reduced below 10 nm. The low \(k\) suggests that a-PnCs can be used as an effective way for tuning thermal transport in amorphous solids. We will also discuss coherent effect in a-PnCs at low temperatures, where thermal transport is dominated by long-wave-length propagons.

Reference
Solid-state thermal rectification, a mechanism in which the magnitude of heat transfer depends on the direction of heat flow, has novel applications in thermal management and nanoscale radiation-based information processing. Several material systems were proposed to achieve this high thermal rectification through radiation. Of particular interest has been the possibility of using phase-transition materials in the thermal near-field. In this talk, we will describe how we demonstrated thermal rectification at the nanoscale between doped Si and VO$_3$ surfaces. In specific, we will show that large differences in heat flow are possible due to the metal-insulator phase transition of VO$_2$. We further show that this rectification increases at systematically controlled nanoscale separations, with a maximum rectification coefficient exceeding 50% at ~140 nm gaps and a temperature difference of 70 K. Our modeling indicates that this high rectification coefficient is due to broadband enhancement of heat transfer between Si and metallic VO$_3$, as compared to narrower-band exchange when VO$_2$ transitions to its insulting state. The results and approaches developed in our work have important implications for probing near-field thermal devices such as diodes and transistors.

**References:**
Phonon Properties of Confined Thin Films Predicted from a Two-Dimensional Lattice Dynamics Framework. Hyun-Young M. King, Bo Fu, Kevin Parrish and Alan McGaughey.

Thermal transport by phonons in thin films can be rigorously described using a two-dimensional (2D) lattice dynamics (LD) framework. This treatment contrasts the standard approach of assuming that the bulk phonon modes obtained from a three-dimensional (3D) treatment exist in the film and of modifying their mean free paths with a phenomenological boundary scattering model.

A mapping algorithm was developed to directly compare 2D and 3D phonon modes and was applied to Lennard-Jones (LJ) argon and multi-layer graphene films described by an optimized Tersoff potential. The algorithm applies a Fourier transform to the polarization vectors of the 2D modes and projects the results onto the cross-plane wave vectors of the 3D modes. A near one-to-one correspondence was discovered at thicknesses of greater than 20 atomic layers for argon and at all thicknesses for graphene. Deviations for the few-layer argon films are attributed to the inherent differences between the 2D and 3D phonon modes, which is primarily caused by the emergence of anisotropy.

Thermal transport in films built from LJ argon and Tersoff silicon was then investigated in the 2D LD framework. Molecular dynamics (MD) simulations were also performed as a benchmark. Thermal conductivity decreases with decreasing film thickness for both the LD and MD calculations, until the thickness reaches eight atomic layers for argon and twelve for silicon. At this point, thermal conductivity increases with a further reduction in thickness due to the increase in low-frequency modes in the phonon density of states. This finding is opposite to the monotonically decreasing trend predicted from the 3D/boundary scattering model approach.
An alternative approach, the Anharmonic Lattice Dynamics (ALD), implementation of the Boltzmann Transport Equation (BTE) has been successfully adopted for the calculation of thermal properties of semiconductors. In this approach, boundary scattering is customarily modeled through Matthiesen’s rule.

Comparing ALD and NEMD on carbon nanostructures, we show that Matthiesen’s rule fails for modeling phonon transport in the quasi-ballistic regime. We then show how implementing boundary conditions in BTE and enhancing the theory with a systematic treatment of the scattering term one can achieve an excellent agreement between NEMD and ALD results. Finally, we demonstrate how accounting for the effects of spatially resolved out of equilibrium phonon distribution, can provide a detailed physical picture of heat transport in the quasi-ballistic regime.

11:15 AM QN04.14.03
Sub-Continuum Air Conduction Measurement Between Si Plates with Surface Features Mohammad Ghashami, James R. Bailey and Keunhan Park; Mechanical Engineering, University of Utah, Salt Lake City, Utah, United States.

The conventional mechanism of heat conduction in the continuum regime is by diffusion processes through random collisions of heat carriers, such as electrons, phonons and molecules. However, when the length scale of a heat transfer domain becomes comparable to or smaller than the mean free path of heat carriers (i.e., sub-continuum regime), ballistic energy transport and boundary scattering behaviours of heat carriers significantly alter the heat conduction mechanism [S. Hamian et al., Int. J. Heat Mass Transf. 80 (2015): 781].

In the present work, we experimentally investigate the diffusive-ballistic heat conduction of air molecules between large planar structures when the gap distance is in the sub-continuum regime. In this regime, heat conduction becomes saturated due to ballistic features while thermal radiation is greatly enhanced due to near-field effects such as photon tunnelling and surface phonon polaritons [R. Messina et al., Phys. Rev. B. 94 (2016): 121410]. The precision measurement of the two heat transfer mechanisms should be made in two scenarios: (1) when there is no participating medium between them (vacuum condition), and (2) when air molecules are present in the gap between the two bodies. The differences in the heat transfer rate between case (1) and (2) should result from the contribution of heat conduction through air molecules. To this end, we will be using an experimental setup based on a nanopositioning platform composed of three piezo-motors, providing six degrees of freedom in x-, y- and z-directions and 1 nm-precision rotational resolution [M. Ghashami et al., Phys. Rev. Lett. 120 (2018): 175901]. The net exchanged power (Qth) can be measured from Pth (i.e., power supply to the heater) required to maintain desired temperature at the hot sample (Tth) for different gap distances while Tc (i.e., cold side temperature) can be maintained by the thermoelectric cooler (TEC) at the bottom. The experimental setup is housed in a vacuum chamber that is capable of controlling the partial vacuum pressure precisely. Varying a partial vacuum pressure can change the mean free path of air molecules, which can demonstrate the role of sub-continuum air conduction in planar configurations. Additionally, the role of the surface condition can be further investigated by manipulating the surface roughness on the samples. The obtained results will help us fundamentally understand the sub-continuum heat conduction physics in a nanoscale gap and its competing effect with the near-field radiative heat transfer.

11:30 AM QN04.14.04

Observations of quasiballistic transport behavior, which occurs if a temperature gradient exists over a length scale comparable to the phonon mean free paths, have recently been reported in numerous thermal characterization experiments using ultrafast laser spectroscopies. However, a precise mapping from these observations to mode-dependent information of phonons is challenging. Here, we will first present a generalized Fourier’s law based on Peierls-Boltzmann transport equation that is able to capture quasiballistic transport behavior in experiments. We will show that misinterpreting the generalized Fourier’s law in experiments would lead to erroneous microscopic information of phonons. Second, we will use this derived generalized Fourier’s law to extract phonon transmission coefficients at solid interfaces using a combination of first principles phonon transport and time-domain thermo-refractance technique. Our work provides a useful perspective on how first principles transport theory can be coupled to experiments to develop deeper physical insights into phonon behaviors.

SESSION QN04.15: Near- and Far-Field Radiation
Session Chairs: Renkun Chen and Bjorn Vermeersch
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 124 A

1:30 PM *QN04.15.01
Scanning Thermal Microscopy—Probing Temperature and Heat Dissipation Down to the Few-Nanometers Scale Eloise Guen1, Antonin M. Massoud1, Ali Alkurdı1, Christophe Lucchesi1, Rodolphe Vailllon1, Valeria Lacatena1, Maciej Haras2, Jean-François Rohillard4, Elyes Nezfaouis3, Jean-Marie Bluet1, Sérène Gomès1 and Pierre-Olivier Chapuis1; 1-CNRS - INSA Lyon, Villeurbanne, France; 2, IES, Madrid, Spain; 3, EMM, Lille, France; 4, ESSEE - ESYCOM, Noisy-le-Grand (Paris region), France.

Scanning thermal microscopy (SThM), a technique derived from atomic force microscopy, is applied with different thermoresistive tips, providing down to 10 nm spatial, few mK temperature, and pW/K thermal conductance resolutions [1].

We first discuss original physical features of the technique. In ambient conditions [2], approach curves unambiguously demonstrate ballistic thermal transport in air. In vacuum, the sample exchange behavior is characterized by means of near-field thermal radiation, however this contribution is observed only under certain particular circumstances which will be discussed. In contact with the sample, SThM is found to be especially applicable for characterizing materials with thermal conductivity lower than 3 W.m-1.K-1, but reduced sample area, as in the case of suspended phononic nanomembranes, can allow characterizing thermal conductivity up to ~50 W.m-1.K-1 [3].

In a second step, recent thermal conductivity and thermal boundary resistance results obtained for various set of samples are highlighted, including thin oxide amorphous films down to the native-oxide case and phononic membranes with partially-perforated holes. Thermal transport mechanisms are discussed, in particular when ballistic phonon dissipation takes place and that simulations based on the Boltzmann transport equation for phonons support the experimental results.


The support of projects QUANTIHEAT (FP7-2012 604668), EFINED (H2020-FETOPEN-1-2016-2017 766853), TIPTOP (ANR-16-CE09-0023), DEMO-NFR-TPV (ANR-16-CE05-0013), THERMOS (INSA-BQR-2017) is acknowledged.

2:00 PM QN04.15.02
Thermal Transport Across Nanoscale Vacuum Gaps—Insights From Lattice Dynamics Calculations Combined with Ab Initio Force Constants Merabia Samy1,2, Ali Alkurdı12, Christophe Adessi1 and Konstantinos Termentzidis2; 1Universite de Lyon, CNRS, UCBL, ILM, Villeurbanne, France; 2INSA Lyon, Villeurbanne, France; CNRS, Villeurbanne, France.

Thermal boundary conductance is basically dictated by phonon transmission at interfaces [1], and an accurate prediction at nanoscale is of a great importance for many applications where thermal management is a vital issue. In microelectronics there is a strong need to know how energy can be exchanged across small vacuum gaps having separation distances of few nanometers. Recent experimental studies reported giant heat flux transfer between gold surfaces at nanometer separation distance [2]. Theoretically, it is expected that at such nanometer distances, heat is exchanged primarily by acoustic waves [3], while radiative heat transfer dominates when the gap is larger than a few nanometers [3].

Thermal transport in the quasi-ballistic regime.

Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 124 A
We have developed a new computational method to probe phonon scattering at interfaces between FCC or diamond like structure materials [4,5]. The idea is to combine lattice dynamics calculations with inputs from ab-initio calculations. Lattice dynamics has been already successfully applied to describe interfacial thermal conductance, but it relies on semi-empirical potentials and lacks the accuracy to describe phonon dispersion curves of bulk materials. Coupling lattice dynamics with interatomic force constants calculated using ab initio calculations opens the way to an accurate description of modal phonon transmission at interfaces.

We used the calculations to probe heat transfer across nanoscale vacuum gaps. We first characterize the thermal conductance due to phonons for silicon/vacuum/silicon and gold/vacuum/gold interfaces [6]. We show that for subnanometric gaps, phonons dominate by far thermal transport even in the presence of air molecules in the gap. Moreover, we demonstrate the major role played by phonon scattering as compared with electron/phonon processes at interfaces [7]. Finally, we compare our ab-initio lattice dynamics results with simplified acoustic mismatch models. We clearly demonstrate that these models fail by several orders of magnitude to describe the thermal conductance across nanoscale gaps. We show that these discrepancies originate from the contribution of intermediate phonon frequencies which are not accurately described by acoustic models.

References

Acknowledgements

Funding from the European Commission H2020-ETFopen project EFINE under grand agreement 756653 is acknowledged.
near-field radiative heat transfer measurements where a set of important parameters are investigated: temperature, geometry and materials. We first consider the configuration of an emitter and a substrate both made of silica, which was already studied in the past but with smaller temperature differences. The large temperature differences (from 100 K to 500 K) allow observing the temperature dependence of near-field radiative heat transfer. Measurements of the near-field conductance are compared to results of the proximity flux (also called Derjaguin) approximation. It is highlighted that the temperature dependence of the exchanged power in the near field is very different to that of the far field, which is another key feature of near field in addition to the distance dependence of the flux.

In a second step, we focus on the influence of the geometry of the substrate on the near-field radiative heat transfer. To do this, we use different patterns (cylinders, lines or grids for examples) etched on a silica substrate, with etching depths ranging from 1 µm to 10 µm, so as to build emitter-substrate distances where the near-field contribution around the patterns is expected to be varying. This experimental work contributes to understanding the behavior of near-field radiation with micron-sized objects smaller than the emitting sphere.

Finally, we investigate the impact of the materials. In particular, indium antimonide (InSb) is investigated as substrate and graphite as emitter. This configuration is attractive for TPV conversion with moderate emitter temperatures (<1000 K) since InSb is a low-energy bandgap material which can be considered for TPV cells [6].

Financial support by the French National Research Agency (ANR) under grant No. ANR-16-CE05-0013 and partial funding by the French "Investment for the Future" program (EquipEx EXTRA, ANR-11-EQPX-0016) and by the Occitanie region are acknowledged.

References
substances, the energy transfer picture based on the lattice vibration, that is, phonon propagation, can be effective like in the ordered solid materials. So far, Sääskilahti, K. et al. (Phys. Rev. B, 90 (2014), 134312; Phys. Rev. E, 93 (2016), 052141) and Zhou, Y. et al. (Phys. Rev. B, 92 (2015), 192505) introduced the spectral decomposition of heat current inside solid materials and the solid-liquid interface for the abovementioned purpose. We newly extended the previous expression for spectral decomposition of heat flux in a frequency regime, which is consistent with the MoP (method of plane) expression for heat flux at a control surface proposed by Torii, D. et al. (J. Chem. Phys., 128 (2008), 044504). Thus, our formulation can be applied to arbitrary molecular systems including soft matters, liquids, and “soft” interfaces like the SAM. In order to validate our formulation, we performed molecular dynamics (MD) simulations on the alkanethiolate SAM and water interface, and the proposed spectrum description of heat flux was applied to this system. As a demonstration, the control surface was located at the middle of the SAM, at which multi-body interactions work among covalently bonded atom sets. It was found that thermal energy is mostly exchanged in the lower frequency bands under 15 THz, in which the characteristic vibrational spectrum of atoms is observed from the VDOS analysis. The cumulative heat flux, which is defined by the spectral heat flux integrated over a frequency, converges to the partial heat flux which is the energy transfer associated with inter- and intramolecular interactions. This fact shows our formulation is consistent with the MoP expression at the control surface as expected. We also applied our method with varying the location of the control surface in the SAM-water system and examined microscopic heat conduction mechanisms in the interface systems in a spectral domain.

4:45 PM QN04.16.05
Spectroscopic Measurements of Heat Transfer at Hybrid Interfaces Using Infrared Pump, Electronic Probe (IPEP) Spectroscopy
Benjamin T. Diroll, Peijun Guo and Richard D. Schaller; NST, Argonne National Laboratory, Lemont, Illinois, United States.

The transfer of thermal energy from the ligand passivating layer to the inorganic core of colloidal nanocrystals is observed using infrared-pump, electronic-probe (IPEP) spectroscopy. Inorganic nanocrystals are excellent model systems for organic-inorganic hybrid interfaces as they have much larger surface-to-volume ratios than bulk solids, which facilitate spectroscopic measurements of weak signals. Such interfaces between disparate materials are challenging to probe by traditional methods. Here, resonant excitation of the hydrocarbon ligand vibrational absorptions results in a transient red-shift of the CdSe nanocrystal excitonic features consistent with heating, as demonstrated by steady-state absorption measurements. The temperature rise can be quantitatively estimated with static absorption/reflection measurements. The time constant associated with heating ranges from 10 ps to 30 ps depending on the sample morphology, static temperature, input fluence, and environment. Although applied here to nanocrystals to measure interfacial heat transfer, IPEP spectroscopy is readily applicable to measure heat transfer with sub-picosecond resolution for any heterogeneous system in which one component has spectrally-isolated molecular vibrations or lattice phonons.

SYMPOSIUM QN05

TUTORIAL: Building Understanding of Phonon Transport—Calculations and Experiment
April 22 - April 22, 2019

* Invited Paper

TUTORIAL
Building Understanding of Phonon Transport—Calculations and Experiment
Monday Afternoon, April 22, 2019
PCC North, 100 Level, Room 124 B

This two-part (theoretical and experimental) afternoon tutorial will dive into topics related to: (1) lattice dynamics and phonon thermal transport calculations and (2) measurements of thermal transport that inform our understanding of underlying phonon behaviors. This tutorial is meant to provide background of state-of-the-art theoretical and experimental techniques used to describe thermal transport in materials.

1:30 PM
Theoretical and Numerical Aspects of Phonon and Lattice Transport Calculations
Lucas R. Lindsay; Oak Ridge National Laboratory

Dr. Lucas Lindsay will cover some of the underlying techniques and challenges of describing lattice thermal transport via Peierls-Boltzmann equation methods coupled with density functional theory. A brief discussion of the development and application of these tools will be given, followed by a deeper dive into the numerics involved and highlights of progress toward addressing current challenges (e.g., temperature and disorder).

3:00 PM BREAK

3:30 PM
Techniques and Challenges Associated with Thermal Transport Measurements Spanning Different Length and Time Scales
Amy Marconnet; Purdue University

Dr. Amy Marconnet will provide an introduction to thermal transport measurement techniques spanning a range of length and time scales. A brief discussion of recent key experimental results that have guided our understanding of phonon transport will be emphasized. Open challenges in the field will be highlighted.

SYMPOSIUM QN05

Emerging Thermal Materials—From Nanoscale to Multiscale Thermal Transport, Energy Conversion, Storage and Thermal Management
April 22 - April 26, 2019

Symposium Organizers
Yongjie Hu, University of California, Los Angeles
Yee Kan Koh, National University of Singapore
Thermal Studies of Nanoporous Thin Films with Increased Periodic Nanopores

Dongehao Xu, Fabian Medina, Yue Xiao and Qing Hao; University of Arizona, Tucson, Arizona, United States.

Nanomaterials introduce new opportunities in tuning the thermal transport for various applications. Among various nanostructured materials, phonon transport within periodic porous structures has been intensively studied for potential applications in thermal management. It is now acknowledged that wave effects of lattice vibrations, i.e., phononic effects, are only important for ultrathin nanoporous structures and at cryogenic temperatures. Experimental evidence is usually found by comparing the thermal conductivities of periodic and aperiodic nanoporous Si films,1,4,5 for measuring the specific heat to justify the phonon dispersion variation.6

In this work, a new approach is proposed to validate the wave effects, simply by comparing the thermal conductivity of the same Si thin film with increased number of nanopores. When phononic effects exist, it is anticipated that the thermal resistance can be largely increased from single to multiple rows of nanopores. Without phononic effects, the thermal resistance of a patterned Si film should linearly increase with the number of nanopore rows. The measured thermal conductivities are compared to frequency-dependent phonon Monte Carlo simulations that assumes incoherent phonon transport and diffusive pore-edge and film-surface phonon scattering.

Reference:

6:30 AM QN05.01.02

Identifying Diels-Alder Reactions for Aqueous Thermal Storage Using Density Functional Theory

Evangelos W. Spotte-Smith1, Peiyuan Yu1, Anubhav Jain4 and Ravi Prasher1,2; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Mechanical Engineering, University of California, Berkeley, California, United States.

Thermal storage offers the potential to reduce the amount of waste heat generated by thermal processes and improve overall energy efficiency. Thermochemical storage using reversible reactions has shown considerable potential for high energy density. However, most current thermochemical systems involve the use of at least one gas phase, thus requiring large volumes and reducing energy density. Condensed-phase, particularly all-liquid, thermochemical storage systems are thus highly desirable in order to improve energy density. In this study, we present a computational search for all-liquid thermochemical storage materials based on the Diels-Alder ([4+2] cycloaddition reactions. Using high-throughput density functional theory (DFT) calculations, we determined the enthalpy change $\Delta H_{\text{rxn}}$, entropy change $\Delta S_{\text{rxn}}$, and turning temperature ($T^* = \Delta H_{\text{rxn}} / \Delta S_{\text{rxn}}$) of 54 Diels-Alder reactions that had been performed in an aqueous solvent in the literature. We screened this test set for turning temperature, identifying nine reactions with a turning temperature close to the working temperature range of water (50 - 150 degrees Celsius). Several of these reactions (the exo-reaction between furen and maleimide and the reaction between furan and acrylonitrile) were selectively modified using functional group substitution to generate additional reactions for study. These modified reactions were predicted to display exceptional thermal properties, increasing the heat capacity of water by as much as 58.7% and improving the thermal energy density of water by as much as 33.8%. Graviometric energy densities as high as 0.5598 MJ/kg were predicted. Experimental work to verify the predicted properties of Diels-Alder reactions are ongoing.

9:15 AM QN05.01.03

Coherent Phonon Transport in a Two-Dimensional Graphene Superstructure

Usama Choudhry, Shengying Yue and Bolin Liao; University of California, Santa Barbara, Santa Barbara, California, United States.

Coherent wave effects of thermal phonons hold promise of transformative opportunities in thermal transport control, but remain largely unexplored due to the small wavelength of thermal phonons, typically below a few nanometers. This small length scale indicates that, instead of artificial phononic crystals, a more promising direction is to examine the wave properties of thermal phonons within hierarchical superstructures matching the thermal phonon wavelength. In this work, we characterize the thermal properties of dodecagraphene (D-[BL1] graphene), a previously unstudied two-dimensional carbon allotrope based upon the traditional graphene structure but containing a secondary, in-plane periodicity. We use density functional theory (DFT) to calculate harmonic and anharmonic interatomic force constants (IFCs), which were then used to calculate the phonon dispersion, scattering rates, group velocities, and lattice thermal conductivity via an iterative solution to the linearized Boltzmann Transport Equation (BTE). We find that despite a very similar atomic structure, D-graphene possesses significantly different thermal properties than that of pristine graphene. At room temperature the calculated thermal conductivity of D-graphene is 600 Wm$^{-1}$K$^{-1}$ compared to 3000 Wm$^{-1}$K$^{-1}$ for graphene. The out of plane acoustic (ZA) mode contribution decreases from 84% in graphene to 47% in D-graphene. We also report a much smaller thermal transport of the presence of three naturally occurring, low frequency optical phonon modes that possess characteristics of phonon answered to arise from a folding of the new acoustic modes and the associated frequency gap opening, a phenomenon also found in superlattices where an out of plane periodicity is introduced. The optical modes make a significant contribution to the thermal conductivity due to enhanced dispersion, comprising over 18% of the thermal conductivity, while the three coherent branches contribute 9% of the total conductivity. The construction of the D-graphene unit cell presents a new method with which the thermal conductivity of 2D materials can be reduced without making drastic changes to its fundamental composition and demonstrates the potential of using coherent phonon effects to significantly modify thermal transport. This work is supported by a Department of Energy Early Career Research Program under award number DE-SC0019244.

9:30 AM QN05.01.04

The Effect of Doping, Vacancies and Isotopes on the Thermal Conductivity of 2D Materials

Kai Xiao, Xufan Li, Yiling Yu, Liangbo Liang, Mina Yoon, Alexander Puretzky, Christopher M. Rouleau and David B. Geohegan; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The heterogeneities such as defects and dopants can give rise to exotic electronic properties in 2D transition metal dichalcogenides (TMDs), but to this date, there is no detailed study to illustrate how heterogeneities can be engineered to tailor their thermal properties. Here, through combined experimental and theoretical approaches, we have explored the effect of defects, doping, and metal isotopes on the thermal transport of monolayer 2D TMDs grown by chemical vapor deposition (CVD). We found that doping and defects in a CVD-grown monolayers 2D crystals can significantly affect their thermal conductivity due to the mass induced kinetic energy and potential energy difference. Furthermore, we...
find the isotopically pure monolayer 2D crystals synthesized by CVD can significantly boost their in-plane thermal conductivity resulting from combined effects of the reduced isotope disorder and a reduction in defect-related scattering. Our work demonstrates that heterogeneity engineering can effectively tune the thermal conductivity of 2D TMDs, which is important for thermal properties development and thermal management in 2D electronic and optoelectronic building blocks.

Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division. Characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:45 AM QN05.01.05
Heat Transport of Anisotropic Nanocellulose Foams Varvara Apostolopoulou Kalkavoura1, Nathalie Lavoine2, Pierre Manier1, Furuta Makito1, Shigian Hu3, Junichiro Shiomi4 and Lennart Bergström1; 1Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden; 2Department of Forest Biomaterials, College of Natural Resources, North Carolina State University, Raleigh, North Carolina, United States; 3Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

Efficient thermal insulation using materials with a small environmental footprint is essential for sustainable thermal management in buildings. Nanocellulose produced from wood cellulose fibers is a nanosized, renewable, light weight cellulose particle of high aspect ratio which exhibits tunable surface properties and low thermal conductivity. We have previously shown that anisotropic nanocellulose foams prepared by directional freezing exhibit lower thermal conductivity than air (=25 mW/mK) perpendicular to the fibers direction at room temperature.

Here, we will present the heat transfer of anisotropic nanocellulose foams as a function of relative humidity (RH) and temperature (T). Hence, we measure the axial and radial thermal conductivities of anisotropic freeze-casted nanocellulose foams by using a customized hot disk thermal constant analyzer at controlled RH and T. Thermal conductivity measurements have been combined with X-ray diffraction and modelling. The strong dependence of the thermal conductivity on the RH will be related to the interaction of the hygroscopic nanocellulose fibrils with water and humidity-dependence of the directional interfacial thermal resistance. We will also address the effect of the crystallinity and alignment of nanocellulose on the thermal conductivity of anisotropic nanocellulose foams.

References

10:00 AM BREAK

SESSION QN05.02: Nanoengineering for Energy Conversion
Session Chairs: Yongjie Hu, Yee Kan Koh, Lucas Lindsay and Amy Marconnet
Monday Morning, April 22, 2019
PCC North, 100 Level, Room 124 B

10:30 AM *QN05.02.01
Transport of Heat, Mass and Charge in Nanostructured Materials Arun Majumdar; Stanford University, Stanford, California, United States.

When materials are nanostructured in the 1-100 nm range, fundamental length scales related to transport are often crossed. In the case of heat transport by phonons, the dominant wavelength at room temperature is typically in the 1-10 nm range. Hence, by nanostructuring to this length scale, thermal transport can be modulated in unprecedented ways. Here I will discuss our observations to reduce thermal conductivity below the “alloy limit” as well as reaching the upper limits of phonon conductance. What has eluded the community is the lower limit, which is likely to occur due to Anderson localization. That is the focus of our current work.

The van der Waals, electrostatic or steric forces between liquid molecules and between liquid-solid interfaces fall in the range of 1-10 nm. When liquids are confined to these length scales, they undergo a variety of transitions that control the liquid, ionic and macromolecular transport, as well as liquid-vapor phase transitions. This talk will discuss what we discovered in nanofluidics, which is forming the basis for new research to probe ions, solvation shells and macromolecules in nanofluidic channels.

Finally, I will discuss our current research to use a new class of oxide material for catalysis of a few redox reactions that are important in energy science. This research will also underscore the need for new experimental probes to study catalysis and surface reactions at nanoscales.

11:00 AM QN05.02.02
On-Sun Testing of a Solar-Thermal Aerogel Receiver Bikram Bhattacharya, Thomas Cooper, Lee Weinstein, Lin Zhao, Elise M. Strobach, Sungwoo Yang, Gang Chen and Evelyn Wang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The performance of line-focus concentrating solar power (CSP) systems, operating at concentrations <100 suns, is limited by receiver thermal losses. Existing linear CSP receivers rely on spectrally selective surfaces enclosed within cylindrical vacuum tubes to minimize heat loss due to radiation and convection. However, using spectrally selective coatings and maintaining a high-quality vacuum at high temperatures (up to 400 °C) increases cost, reduces durability, and restricts receiver geometry to a cylindrical shape. We have developed a solar thermal aerogel receiver comprising of custom-fabricated highly-transparent thermally-insulating silica aerogels that allow transmission of concentrated sunlight, minimization of thermal losses and enables operation in air. We demonstrate the on-sun performance of the prototype aerogel receiver with a 1 m×10 cm aperture area. The prototype receiver consists of seven monolithic solar-transparent aerogel tiles that cover the solar-absorber consisting of a nanopipe loop connected in series and coated with black Pyronark paint. The receiver is paired with a 6 m×6 m linear Fresnel reflector (LFR) array capable of achieving concentration up to 30 suns. Pressurized Dowtherm A is used as the heat transfer fluid which is heated to temperatures up to 350 °C before entering the receiver section. We performed on-sun measurements for different receiver inlet temperatures and incident flux conditions, and report a peak receiver thermal efficiency >65%.

11:15 AM QN05.02.03
All-Ceramic Multilayer Selective Solar Absorbers for Concentrated Solar Power Yang Li, Chongjia Lin, Dezha Li, Shihe Yang and Baoling Huang; HKUST, Kowloon, Hong Kong.

Concentrated solar power (CSP), also known as high-temperature solar-thermal energy conversion, is a promising solar energy harvesting technology due to its efficient sunlight utilization, and high availability in energy storage. For the sake of higher Carnot efficiency and greater cost reduction, next-generation CSP plants are expected to operate at higher temperatures (≥900 K) than those conventional systems. Selective solar absorbers, as the key components in CSP systems, are required to offer high stability and great selectivity at such high temperatures. Selective solar absorbers based on multilayer metal/ceramic thin films are a kind of low-cost and scalable absorbers fabricated by facile processes such as sputtering deposition. However, their thermal stability and spectral selectivity fall behind those state-of-the-art cermets and photonic absorbers. Previously works demonstrated that multilayer absorbers suffered from a variety of high-temperature degradation cases associated with the metal/ceramic interfaces, including delamination, surface oxidation, and atom diffusion.

In this work, we introduced a TiN IR reflector into the multilayer absorbers to replace refractory metals (W, Ta, Mo, etc.) used in conventional designs; meanwhile, another ceramic material, titanium oxy-nitride (TiNO), was utilized as the absorptive layer due to its tunable absorption properties and excellent compatibility with TiN. Two ceramic anti-reflection layers, ZrO2 and SiO2, with gradient refractive indexes were adopted to reduce the surface reflection, and enhance the sunlight absorption. The fabricated all-ceramic absorber displayed highly selective absorption with a high solar absorptance of 91.2% and an ultralow IR emittance of 15.7% at 1000 K. Consequently, a high solar-thermal
conversion efficiency of 82.1% was achieved under the irradiation of 100 suns. This value is on par with or exceeds the record of state-of-the-art selective absorbers. As expected, the all-ceramic absorber was able to sustain its superior performance at high temperatures up to 800 °C. Both SIM-EDX and depth profiles of elements result reveal that the diffusion and oxidation were effectively suppressed in the all-ceramic structure. Moreover, the delamination was also avoided in the ceramic/ceramic interfaces. Compared with previous multilayer absorbers, this all-ceramic absorber boosted the operating temperature of such low-cost multilayer absorbers by ~300 °C, rendering it suitable for the high-temperature applications in next-generation CSP plants.

11:30 AM QN05.02.04
Rational Surface Nanoengineering for Condensation—From Power Generation to Sunlight-Enabled Anti-fogging of Transparent Materials Dimos Poulikakos; Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland.

Thermal processes and materials involving phase change, are practically omnipresent in nature and technology. Viewed in the direction of decreasing temperature, the encountered phase transitions are condensation, freezing and de-sublimation. All share significant scientific challenges in terms of material/surface engineering to control nucleation and growth of the generated phase on a surface, and assure its continuous and facile, passive removal from the surface, to maintain surface functionality and robust performance at a high level, depending on the application of interest. Here, I will focus on the rational, physics-derived, surface nanoengineering, for condensation applications, ranging from power generation targeting high efficiency, to sunlight-driven fogging retardation and rapid defogging of transparent materials.

Enhancing the thermal efficiency of a broad range of condenser devices requires means of achieving sustainable dropwise condensation on metallic surfaces, where heat transfer can be further enhanced by facilitating a reduction in the droplet departure diameter. I will present a novel approach, based on sunlight absorbing metasurfaces, which goes well-beyond state-of-the-art anti-fogging methods such as superhydrophilic coatings. We rationally nanoengineer such transparent metasurfaces, by varying the concentration of embedded plasmonically enhanced light absorbing nanoparticles in an ultra-thin titania film to achieve broadband absorption with tunable transparency. Such surfaces upon illumination induce significant heating at the air-substrate interface where fog is most likely to form and can rapidly de-fog or completely inhibit fog nucleation altogether, Ref. 3. For the same environmental conditions, we demonstrate that such metasurfaces are able to reduce defogging time by up to four-fold compared to reference samples and markedly outperform the most widely implemented solution in anti-fogging, namely, superhydrophilic surfaces. This approach works paves the way for large-scale, low-cost manufacturing that can be applied to a versatile range of materials, including polymers and other flexible substrates, which can further be combined with state-of-the-art technology to overcome remaining impracticalities, safety, and energy-related costs related to fogging.

References:

SESSION QN05.03/QN04.01: Joint Session: Nanoscale and Nonequilibrium Thermal Transport
Session Chair: Ali Shakouri
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 124 B

10:30 AM QN05.03.01/QN04.01.01
Nanoscale Thermal Metrology Using SEM, TEM and Confocal Microscopy Chris Dames 1,2; 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States.

I will review several collaborative efforts at developing new non-contact methods for heating and thermometry at the nanometer scale. Examples include techniques based on SEM (e-beam as a point heater; secondary electron yield as a thermometer), TEM (thermometry using the Debye-Waller effect), and confocal microscopy (luminescence thermometry of individual nanoparticles).

11:00 AM QN05.03.02/QN04.01.02
A Multi-Temperature Model for Non-Equilibrium Thermal Transport Xiulin Ruan; Purdue University, West Lafayette, Indiana, United States.

Conventionally, the two-temperature model has been widely used for electron-phonon coupled non-equilibrium thermal transport. However, many recent applications have shown that different phonon branches can be in strong thermal non-equilibrium. Therefore, assuming a local equilibrium lattice can lead to misleading or wrong results. Here, we present a multi-temperature model to capture the non-equilibrium among different phonon branches, and demonstrate its advantages over the conventional two-temperature model for bulk materials and across interfaces.

11:15 AM QN05.03.03/QN04.01.03
Specular Reflection Creates Lowest Thermal Phonon Conductivity Martin Maldovan; Georgia Institute of Technology, Atlanta, Georgia, United States.

The thermal conductivity of materials is not a fixed physical property but can be manipulated by controlling the transport properties of thermal phonons. Recently, a large number of experiments have been introduced where thermal conduction is reduced by orders of magnitude via phonon mean free path reduction through diffuse surface scattering. In contrast to established work that use the diffuse surface scattering of phonons as the physical mechanism to reduce the thermal conductivities, in this talk we show that the largest reduction of thin film heat conduction is achieved via specular scattering. Our results thus create a new paradigm for heat conduction manipulation since smooth surfaces – in contrast to rough surfaces – can be more effective on suppressing thin film phonon heat conduction.

11:30 AM QN05.03.04/QN04.01.04
Phonon Heat Conduction and Nanoscale Disorder—From Scatterings to Localizations Sebastian Volz; CNRS–University of Tokyo, Tokyo, Japan.

Effect of structural disorder on phonon thermal conduction remains an open question with a large spectrum of physical effects, as the plane-wave description of atomic vibrations is expected to become irrelevant. In a first stage, atomic scale disorder will be investigated in various systems – silicon [1], SiGe nanowires [2], partial-crystal partial-liquid [3], 2D [4,5] - with atomic scale simulations. Secondly, thermal properties of nanoscale random materials [6,7] will be presented to raise the question of the eventual impact of localization on heat conduction.

Molecular Engineered Polymer with High Thermal Conductivity

Polymers have entered almost every aspect of modern life, from packaging and soft robotics to aerospace sector and 3D printing. Traditional polymers are both electrically and thermally insulating. The discovery and development of electrically conductive polymers has led to innovative electronic applications such as flexible displays, wearable biosensors and lightweight photovoltaics. As in the case of electrically conductive polymers, the development of thermally conductive polymers would open up a range of advanced thermal applications including an emerging self-cooling system to existing electronics casings. This talk will summarize our recent work on improving thermal conductivity of polymers. We developed scalable polyethylene films with thermal conductivity ~62 W/mK by extrusion and roll-to-roll drawing processes. Structural studies and thermal modeling reveal that the film consists of nanoparticles with crystalline and amorphous regions, and the amorphous region has a remarkably high thermal conductivity of ~16 W/mK. We grew thermally conductive conjugated polymer by bottom-up oxidative chemical vapor deposition technique, and realized high thermal conductivity ~2.2 W/mK in conjugated polymer (P3HT) thin film by engineering both inter- and intramolecular interactions and taking advantage of both strong C=C covalent bonding along the extended polymer chain and strong π-π stacking noncovalent interactions between chains. We will also discuss our current work on enhancing heat conduction in hydrogels. This work is supported by Department of Energy—Basic Energy Sciences under award number DE-FG02-02ER45977.

D.B. acknowledges support from the Office of Naval Research MURI, Grant No. N00014-16-1-2436.

References:

Optical phonon linewidth is crucial to infrared dielectric function of polar materials and thermal conductivity of certain materials that have a large number of optical phonon branches. The current understanding of optical phonon linewidth is associated with three-phonon scattering. In this work, however, we show that four-phonon scattering can dominate the optical phonon linewidth and infrared optical properties at elevated temperatures for a range of important materials, including cubic boron arsenide (BAs), cubic silicon carbide (3C-SiC), and α-quartz. Strikingly, in large band gap-materials, e.g., BAs and AlSb, four-phonon scattering rates are found to be orders of magnitude higher than three-phonon scattering rates even at room temperature. The predicted infrared optical properties of α-quartz after including four-phonon scattering can well explain experimental measurements.

Heat dissipation has become an increasingly important technological challenge in modern electronics. Discovering new high thermal conductivity materials that can efficiently dissipate heat from hot spots and improve device performance are urgently needed. In this talk, I will describe our recent progress in developing emerging high thermal conductivity semiconductors including boron arsenide (BAs) and boron phosphide (BP). We synthesized BAs and BP single crystals without detectable defects, and measured a room temperature thermal conductivity of 1300 W/mK [1] and 500 W/mK [2] respectively. Our ultrafast spectroscopy study in conjunction with atomistic theory reveals that the unique band structure of BAs allows for very long phonon mean free paths and strong high-order anharmonicity through the four-phonon process. The single-crystal BAs has the highest thermal properties among all common metals and semiconductors. In addition, I will briefly discuss our efforts in characterizing thermal boundary resistance and integrating BAs and BP with high-power electronics for near-junction thermal management applications through the combination of measurement and atomistic simulations. Our study establishes BAs and BP as new benchmark materials for thermal management applications, and exemplifies the power of combining experiments and ab initio theory in new materials discovery.

References:
Condensation and boiling are integral processes in many industrial applications including power generation, HVAC, and thermal management of electronic systems. Current efforts aimed at increasing heat transfer during these processes predominantly focus on altering either the chemistry or the texture of the solid-fluid interface. In this talk we will expand beyond these two design variables and will discuss how softening of these surfaces impacts droptime condensation [1] and nucleate boiling [2]. An intriguing component of these phase change processes on soft surfaces is that both microscale droplets and bubbles can significantly deform such materials through Laplace pressure and capillary force at the triple phase contact line. We first discuss how these elastocapillary processes impact heat transfer during condensation across individual droplets as well as their nucleation, growth, and shedding. By integrating these trends over droplet population, we show that softening of the surfaces below shear modulus of about 500 kPa is detrimental to dropwise condensation. In contrast, we use theoretical arguments to show that softening of the surface could significantly facilitate onset of nucleate boiling (ONB). Specifically, we use classic kinetic theory to show that softening of a smooth-surface could mildly decrease superheat needed for ONB. We also discuss a close-form model of vapor trapping and bubble seeding from soft surfaces with conical cavities to show that superheat needed for ONB decreases linearly with shear modulus of the surface. Thus, our work shows that boiling could be manipulated using mechanical properties of the surface. We will also briefly discuss practicalities involved in implementing soft surfaces in boilers and some of the remaining outstanding fundamental questions.


A novel solar heating (SH) and radiative cooling (RC) system based on black surface with selective cover (BS-S) is proposed. This system can provide heat via photothermal conversion and obtain cooling energy by radiative cooling. Photonic approach is applied to design selective cover for SH-RC system. The selective rigid cover consists of a 500 μm-thick zinc sulfide (ZnS) substrate and alternating layers of ZnS and ytterbium fluoride (YbF3) with varying thicknesses. It has strong and remarkably spectral selective characteristics. The transmissivity in SH band (i.e., 0.3–2.5 μm) and RC band (i.e., 8–13 μm) is approximately 0.85, the reflectivity in wavelength band 3–8 μm is approximately 0.70. With the selective rigid cover, air pressure between the cover and black surface could be low (maybe even vacuum) to suppress heat conduction and heat conduction. Numerical analysis demonstrates that in SH process, when surface temperature is 80 °C, the vacuum BS-S case shows a thermal efficiency of 45.9%, approximately 11.5% higher than that of the typical air pocket BS-S case. In RC process, the equilibrium temperature of the vacuum BS-S case and the typical air pocket BS-S case are lower than those of ambient air by approximately 28.9 °C and 22.5 °C, respectively. This selective rigid cover provides an alternative choice for integrating combined SH-RC system and has potential to enhance the performance of the diurnal solar heating and nocturnal radiative cooling processes.

Liquid-vapor phase change is essential in many applications including water purification, power generation, and thermal management. However, effectively utilizing these processes requires detailed understanding and manipulation of interfacial transport. In the first part of the talk, we discuss evaporation from ultra-thin nanoporous membranes.
Tunable Thermal Transport and Reversible Thermal Conductivity Switching in Topologically Networked Bio-Inspired Materials

simultaneously when coated on various IR reflectors, including Au, stainless steel, Al, and TiN. Particularly, the absorbers with Au reflectors exhibited a high solar absorptance of perhydropolysilazane (PHPS) solution, acted as the protection and anti-reflection coating. Both full-spectrum sunlight absorption and strong IR reflection were achieved resonance wavelengths. Due to the in-plane plasmonic coupling of adjacent TiN nanoparticles, the resonance wavelength was able to red-shift to near-infrared (NIR) range. As a switch, offering the possibility of engineering thermally conductive biological materials with dynamic responsivity to heat. This on/off ratio in thermal conductivity switching is over a factor of three larger than the current state-of-the-art thermal atomic vibrations. By varying the network topology, or crosslinked structure, of squid ring teeth-based bio-polymers through tandem-repetition of DNA sequences, we show that modulate the thermal conductivity of topologically networked materials by nearly a factor of four following hydration, through manipulation of the displacement amplitude of conductivity switches have resulted in only modest on/off ratios, since only a relatively narrow portion of the phononic spectrum is impacted. Here, we report on the ability to augment the thermal conductivity of topologically networked materials with dynamic responsivity to heat.

A Framework for Continuum Simulations of Interfacial Phase Change Processes Anirban Chandra1, Pawel Keblinski1, Onkar Sahni1 and Assad A. Oberai2; Rensselaer Polytechnic Institute, Troy, New York, United States; University of Southern California, Los Angeles, California, United States.

Continuum-scale simulations of phase change processes are essential for assisting the design of engineering systems, such as heat pipes and combustion chambers. To quantitatively predict the rate of the phase change in micro-scale systems it is imperative to properly account for the boundary conditions at the interface between phases. For example, in liquid-vapor phase change simulations, the typical continuum assumptions are, a) temperature is continuous at the interface, and b) vapor density near the interface is equal to the saturated density. Results of molecular dynamics (MD) simulations have indicated that in many situations such assumptions are not satisfied. To address these issues, we present a framework for continuum simulations capable of relaxing the aforementioned assumptions. We use finite elements to solve the Navier-Stokes equations while correctly accounting for the flux jump conditions at the interface. Expressions for phase change rates and temperature jumps are obtained from theoretical considerations and augmented by MD simulations. Problems including the burning of solid propellants and evaporation/condensation of liquids are discussed.

High-Performance Solution-Processed TiN/SiOx Selective Absorbers for Solar Thermophotovoltaic Energy Conversion Yang Li, Chongjia Lin and Baoling Huang; Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong.

Solar thermophotovoltaic (STPV) systems, which leverage the benefits of both solar-thermal and photovoltaic (PV) technologies, involve efficient and dispachable approaches to generating electricity. The key components in a STPV system include a selective solar absorber, a selective emitter, and a solar cell at least. The total input power of a STPV system is determined by the sunlight absorption efficiency of the selective absorber. Considering the high operating temperatures of STPV systems, selective absorbers are required to maintain high absorption for solar radiation and low emission beyond a cut-off wavelength in the infrared region to avoid thermal re-radiation even at elevated temperatures. To date, almost all the state-of-the-art selective absorbers/emitters such as cermets and photonic crystals with superior performance (i.e., high selectivity and high thermal stability) were generally manufactured with complicated and expensive micro-fabrication or nano-fabrication techniques, leading to high cost and challenges for large-scale production. Moreover, the obtained absorbers/emitters often encounter problems when being integrated with solution-processed solar cells. Therefore, developing high-performance solution-processed absorbers/emitters is urgently demanded.

Tunable Thermal Transport and Reversible Thermal Conductivity Switching in Topologically Networked Bio-Inspired Materials John A. Temple1, Abdon Pena-Francesch2, Huhun Jung2, Madhusudan Tyagi3, Benjamin Allen2, Melik Demirel2 and Patrick Hopkins1; 1University of Virginia, Charlottesville, Virginia, United States; 2The Pennsylvania State University, University Park, Pennsylvania, United States; 3Max Planck Institute for Intelligent Systems, Stuttgart, Germany; 4NIST Center for Neutron Research, Gaithersburg, Maryland, United States.

The dynamic control of thermal transport properties in solids must satisfy the fact that phonons are inherently broad-band. Thus, efforts to create reversible thermal conductivity switches have resulted in only modest on/off ratios, since only a relatively narrow portion of the phononic spectrum is impacted. Here, we report on the ability to modulate the thermal conductivity of topologically networked materials nearly by a factor of four following hydration, through manipulation of the displacement amplitude of atomic vibrations. By varying the network topology, or crosslinked structure, of squid ring teeth-based bio-polymers through tandem-replication of DNA sequences, we show that this thermal switching ratio can be directly programmed. This on/off ratio in thermal conductivity switching is over a factor of three larger than the current state-of-the-art thermal switch, offering the possibility of engineering thermally conductive biological materials with dynamic responsivity to heat.


Effective system energy management and cooling solutions is critical for a range of increasingly complex systems and missions. Various industries and agencies seek technologies and design techniques to cool ultra-high heat fluxes in various applications, and thereby increase system energy efficiencies in future advanced lasers, radars and power electronics. There has been an increasing interest in exploiting the use of additive manufacturing in developing nontraditional cooling schemes to be built directly into components. This study investigates the heat transfer and pressure loss performance of additively manufactured micro-channel heat exchanger. A heat exchanger of 30 micro-sized channels was manufactured via the Direct Metal Laser Sintering (DMLS) method and tested at a range of Reynolds numbers. Same test setup and configurations have been used to test the DMLS manufactured micro-channel heat exchanger, and the results are compared to the mini-channel heat exchanger of similar dimension but manufactured traditionally. The results have shown that although DMLS manufactured micro-channel heat exchanger yield a higher-pressure loss, it has shown significantly improved convective heat transfer compared to the mini-channel heat exchanger tested under same conditions but fabricated traditionally. It is likely that non-post processed surface of the DMLS manufactured micro-channels is the main contributor of this augmented heat transfer. Future study is needed to further understand the mechanisms behind the phenomena observed here.
Lithium-ion batteries (LIB) have found a wide range of applications in many consumer products in the last 25 years. In particular, Navy and Marine Corps has various applications using LIB and safe battery technologies are critically needed. One of the most important safety considerations for LIB cells is thermal stability under various abuses such as exposure to heat, nail penetration, external short circuit, crushing, and so on. Several exothermic reactions can occur as the inner cell temperature is increasing, and if the heat generation is larger than the dissipated heat to the surroundings, this leads to heat accumulation in the cell and acceleration of the chemical reactions, which can then lead to a thermal runaway. Since the behavior of batteries is strongly affected by the interaction of physics on varying length and time scales: a multi-physics and multi-scale model is needed to simulate this process. While many approaches have been reported in literature, they are not directly applicable in large-format LIB cells and the development of multi-scale and multi-physics models are relatively limited and still computational expensive. For example, in large formatted battery cells, the uniformity of the electrical potential along the current collectors in the cell composites is no longer given. Additionally, due to the inhomogeneity of the distribution of the temperature field with respect to the cell geometry, thermal dynamics must also be taken into account. This study reports the recently developed multi-scale and multi-physics model for simulating the thermal runaway inside a large-format Lithium-ion battery using COMSOL software. For the electrochemical processes, the porous electrode theory with contributions coming from exothermic side reactions is used to model abuse mechanisms, which could lead to a thermal runaway. For the thermal-mechanical processes, models of thermal abuse reactions that occur at specific elevated temperatures have been simulated. Prior experimental data on a large-scale lithium-ion battery tested at NSWCCD has been used to construct and validate the model with good agreement.

Manipulating heat conduction is an appealing thermophysical problem with enormous practical implications, which requires insights into the lattice dynamics. Strain engineering is one of the most promising and effective routes towards continuously tuning the thermal transport properties of materials due to the flexibility and robustness. However, previous studies mainly focused on quantifying how the thermal conductivity is affected by strain, while the fundamental understanding on the electronic origin of why the thermal conductivity can be modulated by mechanical strain has yet to be explored. In this talk, I would like to present our comparative study of thermal transport in two-dimensional group III-nitrides (h-BN, h-AlN, h-GaN) and graphene. Although the monolayer group III-nitrides possess similar planar honeycomb structure with graphene, their thermal conductivity is substantially lower and the root reason cannot be intuitively attributed to the mass difference. We then establish a microscopic picture to connect phonon anharmonicity and lone-pair electrons. Direct evidence is provided for the interaction between lone-pair electrons and bonding electrons of adjacent atoms based on the analysis of orbital-projected electronic structures, which demonstrates how nonlinear restoring forces arise from atomic motions and lead to strong phonon anharmonicity. The microscopic picture of lone-pair electrons driving strong phonon anharmonicity provides coherent understanding of the diverse thermal transport properties of the monolayer group III-nitrides compared to graphene. Furthermore, the thermal conductivity (κ) of planar monolayer group III-nitrides is unexpectedly enlarged by up to one order of magnitude with bilateral tensile strain applied, which is in sharp contrast to the strain induced κ reduction in graphene despite their similar planar honeycomb structure. The anomalous positive response of κ to tensile strain is attributed to the attenuated interaction between the lone-pair electrons around N atoms and the bonding electrons of neighboring (B/Al/Ga) atoms, which reduces phonon anharmonicity. The microscopic picture for the lone-pair electrons driving phonon anharmonicity established from the fundamental level of electronic structure deepens our understanding of phonon transport in 2D materials and would also have great impact on future research in micro-/nanoscale thermal transport such as materials design with targeted thermal transport properties.

We report the electrothermal properties of AZO/Ag/AZO (AAA) trilayer on PET, which helped us develop a low cost high performance transparent flexible electrode and heater (TFEH) using RF magnetron sputtering. The thickness of the Ag interlayer (~5-7.5 nm) in the AAA trilayer was varied, and its electrical, optical and structural properties was thoroughly investigated. At optimized Ag interlayer thickness of 5 nm, the AAA trilayer based TFEH yielded saturation temperatures beyond 100 °C at 10 V which makes it a suitable energy efficient device. The time dependent temperature profile along with its highly stable and reversible thermal behavior demonstrated that it is a promising low cost TFEH device that can be developed industrially on large areas using RF magnetron sputtering. Most importantly the AAA trilayer based TFEH provides a high-performance alternative to the conventional ITO electrodes at a much lower cost.

We present new composite with significantly improved Thermal Conductivity (TC) that comprises a continuous network of thermally conductive fillers and a natural polyl. The network of thermally conductive filler, in this case boron nitride nanosheets (BNNS), was an aerogel that was fabricated with the ice template method. Subsequently, the aerogel was carbonized and filled with xylitol with help of vacuum infiltration of liquefied xylitol. The aerogel provided a 3D thermal conductive pathway and also acted as a scaffold to form a network of thermally conductive filler, in this case boron nitride nanosheets (BNNS), was an aerogel that was fabricated with the ice template method. Subsequently, the aerogel was carbonized and filled with xylitol with help of vacuum infiltration of liquefied xylitol. The aerogel provided a 3D thermal conductive pathway and also acted as a scaffold to provide the oriented crystallization of xylitol. Our results demonstrate that the BNNS scaffold and packing of oriented xylitol crystals play a key role in improving TC of the composite. With BNNS content of 18.16 wt% (6.14 vol %) TC of above 4.5 W/mK, which is higher than that reported in recent literatures, was obtained.

Van der Waals Confinement Enhances Phonon Transport by Reducing Atomic Thermal Displacement Magnitudes Xiaoxiang Yu1, Dengke Ma1, Chengcheng Deng1, Xiao Wan1, Meng An1, Han Meng1, Xiaobo Li1, Xiaoming Huang1, and Nuo Yang1; 1Huazhong University of Science and Technology, Wuhan, China; 2Shaanxi University of Science and Technology, Xi’an, China.

The van der Waals (vdW) interactions exist in reality universally and play an important role in physics. Here, we show the study on the mechanism of vdW interactions on phonon transport in atomic scale, which would boost developments in heat management and energy conversion. Commonly, the vdw interactions are regarded as a hindrance in phonon...
transport. Here, we propose that the vdW confinement will enhance phonon transport. Through molecular dynamics simulations, it shows that the vdW confinement makes more than two-fold enhancement on thermal conductivity of both polyeleynyl single chain and graphene nanoribbon. The quantitative analyses of morphology, local vdW potential energy and dynamical properties are carried out to reveal the underlying physical mechanism. It is found that the confined vdW potential barriers reduce the atomic thermal displacement magnitudes, thus lead to less phonon scattering and facilitate thermal transport. Our study offers a new strategy to modulate the heat transport.

QN05.06.11
Effect of Pressure on Thermal Conductivity of Oxide Glasses Jihui Nie, Siddharth Sundararaman, Liping Huang and Pawel Keblinski; Rensselaer Polytechnic Institute, Troy, New York, United States.

We use molecular dynamics simulations to determine the pressure-induced structural changes in several oxide glasses including permanent densification and the effect of these changes on thermal properties. We show that densified glass structures exhibit increased thermal conductivity, which may be attributed to the increased density and elastic modulus. The local properties analysis reveals that the higher-pressure treatment reduces elastic heterogeneities, which might also contribute to higher thermal conductivity of densified glasses.

QN05.06.12
Electrical, Optical and Thermal Properties of Different Metal Doped Zinc Oxide Thin Film for Flexible Transparent Heater Jasmine Beckford, Monree K. Roul, Makkes K. Behera, Kelsey Yarbrough, Sangram K. Pradhan and Messiah Bahoura; Norfolk State University, Norfolk, Virginia, United States.

Gallium doped zinc oxide (GZO) and Aluminum doped zinc oxide (AZO) thin films were often grown on substrates such as glass, flexible polyethylene terephthalate substrate through using physical vapor deposition technique. The thin films were ultra-smooth in nature and showed outstanding optical, and electrical properties. Highly compact and dense PLD target was made in the laboratory fromAl2O3, Ga2O3 and ZnO powder in an appropriate proportion with a less than 10 atomic weight percentages of Ga and Al followed by isotropic press as well as high temperature annealing (1200 °C) for 12 hours. AZO thin films show stable and reproducible Joule heating effect of more than 100°C by the application of low (~10 V) voltages. GZO transparent heater also showed a stable and reproducible Joule heating effect and the temperature can reach easily close to the 100°C by the application of low input (8V) voltages. The samples showed low resistivity of about 2.6×10⁻³ Ω cm and 3.7×10⁻³ Ω cm and also exhibited high optical transparency value in the visible region of the electromagnetic spectrum. The temperature dependent resistivity behavior of the films were investigated using four-point probe technique. This exciting results encourages the use of GZO and AZO transparent oxide in different optoelectronics device application.

QN05.06.13
Thermal Conductivity Tuning in Drilling Fluid by Bentonite Functionalization SungHyun Hong and Soo Young Kim; Chung-Ang University, Seoul, Korea (the Republic of).

Advances in nanotechnology have contributed to dramatically increasing the thermal conductivity of fluids. Nanoparticles with high thermal conductivity have a high surface area relative to their mass and thus increase the thermal conductivity of the fluid more efficiently with a small amount of addition. However, unlike a pure solution such as DI water, complex fluids such as drilling mud have a large influence of other components so not too much increase the thermal conductivity through the addition of nanoparticles. Therefore, we do not simply add nanoparticles but use a method to increase the thermal conductivity by growing ceramics with high thermal conductivity directly on the solid particle surface added to the complex fluid. Synthesis of nanoparticles using the conventional bottom-up method was inferior in terms of cost and yield compared to synthesizing nanoparticles in a top-down method. But it is expected that only small amounts of nanoparticles will have a great effect, if the particles are synthesized only on the surface of the other particles by the bottom-up method. We made drilling mud after functionalization of ceramics (BN, SiC, MoS₂, WS₂) with high thermal conductivity on bentonite surface which is the most important additive substance to drilling mud. Thermal conductivity of the drilling mud was compared with the conventional method in which the same amounts of nanoparticles were simply mixed in the conventional method in which the same amounts of nanoparticles were simply mixed in the drilling mud. We also measured the FE-SEM, RAMAN, and XPS to check the growth of the particles on the bentonite surface and measured the viscosity according to the flow rate to confirm the performance as a drilling mud. We report how to increase the thermal conductivity of a complex fluid in a different way than previously.

QN05.06.14
Thermal Properties of Binary Filler Composites with Graphene and Boron Nitride Jacob S. Lewis, Andres Sanchez Magana, Sahar Naghibi, Zahra Barani, Ruben Salgado, Fariborz Kargar and Alexander A. Balandin; Phonon Optimized Engineered Materials (POEM) Center, Department of Electrical and Computer Engineering, Materials Science and Engineering Program, Bourns College of Engineering, University of California, Riverside, California, United States.

The exceptionally high thermal conductivity of graphene has driven interest toward its applications in thermal interface materials (TIMs) [1-3]. In addition to its unique heat conduction properties, graphene is also a strong conductor of electricity, which is problematic for certain TIM applications where electrical insulation is paramount. A common strategy for the optimization of composite materials is to combine two or more different thermally conductive fillers. Typically, work along this vein employs fillers of disparate size, shape, and aspect ratios with the larger-sized fillers providing the greatest contribution of overall thermal transport and the smaller fillers improving the interstitial thermal transport between the larger fillers. Unlike much of the previous work into binary fillers, we report on polymer composites filled with few-layer graphene and hexagonal boron nitride (h-BN) of similar lateral dimensions, thicknesses, and aspect ratios. In each filler material, phonons are the primary heat carrier, necessitating the selection of lateral dimensions larger than the “gray” phonon mean free path (MFP) in the micrometer distance range. The composition and structure of the resulting epoxy-based composites were verified using scanning electron microscopy (SEM), Raman, and Brillouin spectroscopy. Thermal measurements were conducted using the “laser flash” techniques. It was found that the use of electrically conductive graphene and electrically insulating h-BN fillers of similar physical dimensions can be complementarily leveraged to achieve an independent control of the thermal and electrical conductivity of the TIM. Varying the constituent fraction of graphene in composites with ~44% filler loading can tune the thermal conductivity enhancement from a factor of ~15 to ~34 while changing the electrical resistivity from 3×10⁴ Ω-mm to 10⁵ Ω-mm, i.e. spanning the resistivity range from an insulator to a conductor. We offer an analytical model of a factor that describes the experimental thermal conductivity data of the binary filler composites. The obtained results are illustrative of a promising strategy for the development of next-generation thermal interface materials with specific control of electrical properties, allowing for the expression of electrically insulating or electrically grounding behaviors.


QN05.06.15
Phononic Topological Insulators Based on Six-Petal Holley Silicon Zao Yu, Ren Ren and Jaeho Lee; University of California, Irvine, Irvine, California, United States.

Since the discovery of the Quantum Spin Hall Effect, electronic and photonic topological insulators have made substantial progress, but phononic topological insulators in solids have received relatively little attention due to challenges in realizing topological states without spin-like degrees of freedom and with transverse photon polarizations. Here we present a holley silicon-based phononic topological insulator design, in which simple geometric control enables topologically protected in-plane elastic wave propagation up to GHz ranges when the unit cell reaches submicron scales. By incorporating a hexagonal lattice of six small holes with one large hole in the center and by creating a hexagonal lattice by themselves, the six-petal holley silicon, which has C₆ symmetry, induces zone folding to form a double Dirac cone. Based on the hole dimensions, breaking the discrete translational symmetry allows the six-petal holey silicon to achieve the topological phase transition, yielding two topologically distinct phononic crystals. Based on the unit cell periodicity, the transition readily shifts from low- to high-frequency ranges. Our numerical simulations confirm inverted band structures and show backscattering-immune elastic wave transmission up to 90% at 14.83 GHz through defects including a cavity, a disorder, and sharp bends when the unit cell periodicity is 500x3 nm. The six-petal holey silicon design also offers robustness against geometric errors and potential fabrication issues such as over- or under-etching. The simulations of the six-petal holey silicon with the same periodicity show up to 90 % transmission of elastic waves at 13.8 and 15.37 GHz even when the holes are under-sized by 5 % or over-sized by 2.5 %, respectively, in which the shift of bandgap is led by the change of porosity. These findings provide a detailed understanding of the relationship between geometry and topological properties and pave the way for the development of next-generation elastic wave devices.
Spectral emissivity control is critical for optical and thermal management in the ambient environment because solar irradiance and atmospheric transmissions occur at distinct wavelength regions. For instance, selective emitters with low emissivity in the solar spectrum but high emissivity in the mid-infrared can lead to significant radiative cooling. Ambient variations require not only spectral control but also a mechanism to adjust the emissivity. However, most selective emitters are fixed to specific wavelength ranges and lack dynamic control mechanisms. Here we show ultraviolet to mid-infrared emissivity control by mechanically reconfiguring graphene, in which stretching and releasing induce dynamic topographic changes. We fabricate crumpled graphenes with pitches ranging from 40 nm to 10 μm using deformable substrates. Our measurements and computations show that 290-nm-pitch crumpled graphene offers ultraviolet emissivity control in 200-300 nm wavelengths whereas 10-μm-pitch crumpled graphene offers mid-infrared emissivity control in 7-19 μm wavelengths. Significant emissivity changes arise from interference induced by the periodic topography and selective transmissivity reductions. Dynamic stretching and releasing of 290-nm- and 10-μm-pitch crumpled graphene show reversible emissivity peak changes at 250 nm and at 9.9 μm wavelengths, respectively. This work demonstrates the unique potential of crumpled graphene as a reconfigurable optical and thermal management platform.

Plasmonic nanostructures generate heat via the photothermal effect when excited with a specific wavelength of light, where optically excited surface plasmons decay to produce hot electrons that subsequently couple to the lattice vibrations. Photothermal cancer therapy shows promise as an application using this effect, where local hyperthermia leads to cell death. However, noble metal nanoparticles traditionally used in plasmonic applications exhibit surface plasmon resonance in the lower-wavelength visible range, where human tissue is not transparent. As a result, recent research efforts have pushed new plasmonic nanostructures and materials into the near- and mid-infrared ranges by using anisotropic geometries. Gold nanorods are extensively used due to their wavelength tunability of the plasmon resonance and their ability to be modified and functionalized for specific binding, enhanced detection, and drug delivery. The thermal transport of this system at the cellular level is not heavily studied, therefore we experimentally measure the thermal transport in a system of cancer cells infiltrated with gold nanorods in vitro at various concentrations, to understand the minimum illumination intensities and durations required for cancer cell death. We report, for the first time, the interfacial thermal conductance between gold nanorods and the ovarian cancer cellular environment as measured by ultrafast pump-probe laser techniques. We also report the thermal conductivity and heat capacity of the cancer cells. By understanding the thermal properties of this system, more defined and tailored photothermal therapy regimens are made possible. This study also provides an experimental framework for measuring the thermal properties of other photothermal therapy agents in cellular environments in the future.

Anisotropic Thermal Conductivity in the Polycrystalline Environmental Barrier Coating γ-YSi3O7: David Olson, Cory Parkers, Valentina Avincolatri, John Gaskis, Elizabeth Opilar and Patrick Hopkins; 1University of Virginias, Charlottesville, Virginia, United States; 2Materials Science and Engineering, University of Virginia, Charlottesville, Virginia, United States; 3Physics, University of Virginia, Charlottesville, Virginia, United States.

Aerospace applications in which high heat fluxes are reached necessitate the use of unique materials to withstand these harsh environments. The need for environmental barrier coatings (EBCs) are of particular importance in limiting the oxidation of aerospace components and the volatility of the SiO2 scale commonly found in silicon-based ceramic coatings. Rare earth mono- and disilicates have been identified as promising EBCs due to their ease of application via various plasma spray processes. However, a robust examination of the insulating thermal properties of these systems has yet to be performed. To better understand the thermal processes and anisotropy associated with these disilicates, we examine the commonly used polymorph of yttrium disilicate, γ-YSi3O7. Using a combination of time- and frequency-domain thermoreflectance, we compare the extracted thermal conductivity maps to associated electron backscatter diffraction micrographs. The thermal conductivity maps exhibit strong anisotropy in the monoclinic structure, in good agreement with other anisotropic features of the system. The results are significant in that they are the first experimental measurements of the anisotropic thermal conductivity in a thermal barrier coating, and should provide a basis for plasma-based applications in which the potential for texturing is strong.

Tunable Functionality of High Entropy Carbide Thin Films via Carbon Stoichiometry: Christina Rost, Trent Bormann, Mohammad Hossain, Jon-Paul Marzia and Patrick Hopkins; 1University of Virginia, Charlottesville, Virginia, United States; 2Materials Science & Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

Materials science is challenged with developing new materials in order to meet the demands of technological innovation. Consequently, this opens the door to novel or complex properties awaiting exploration. High entropy carbides (HECs) continue to demonstrate the viability of materials engineering using configurational entropy to aid in phase development. Using two compositions, Hf-Nb-Ta-Ti-Zr-C (HEC3) and Hf-Mo-Ta-W-Zr-C (HEC6), we explore the thermal transport properties of these systems as carbon stoichiometry is varied. Using time domain thermoreflectance (TDR), we measure thermal conductivity of both the HEC3 and HEC6 thin film series and then relate trends to other observed characteristics of each system such as electrical conductivity, crystallinity, and modulus. Total thermal conductivity systematically varies with increasing deposition flow rate of methane, while the electrical contribution to the thermal conductivity decreases. Results are discussed in terms of various scattering mechanisms from different types of defects, emphasizing understanding of thermal properties from both a local and a global structural perspective. In this talk we focus on the experimental process of elimination using several metrology techniques in conjunction with TDR to gain meaningful perspective on configurationally disordered, highly crystalline systems.

Observation of Second Sound in Graphite At Temperatures Up to 100 K Bryan A. Duncan, Samuel Huberman, Ke Chen, Bai Song, Vazrik Chiloyan, Zhiwei Ding, Alexei Maznev, Gang Chen and Keith Nelson; 1Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Wave-like thermal transport in solids, referred to as second sound, has until now been a exotic phenomenon limited to a handful of materials at low temperatures. This has restricted interest in its occurrence and in its potential applications. Through time-resolved optical measurements of thermal transport on 5-20 μm length scales in graphite, we have made direct observations of second sound at temperatures above 100 K. The results are in qualitative agreement with ab initio calculations that predict wavelike phonon hydrodynamics on ~ 1-μm length scale up to almost room temperature. The results suggest an important role of second sound in microscale transient heat transport in two-dimensional and layered materials in a wide temperature range.

Mitigation of Point-Contact Thermal Boundary Resistance in Elastomeric Composites Through Liquid Metal-Bridged Tungsten Fillers Wilson Kong, Matthew Ralphs, Robert Wang and Konrad Rykaczewski; Arizona State University, Tempe, Arizona, United States.

As increasingly powerful microelectronic chips shrink in size and scale, inadequate waste heat dissipation ultimately results in poor computational performance or early device failure. Therefore, advances in thermal interface materials (TIMs) are necessary in combating detrimental heating issues by providing improved avenues for thermal transport. Many types of polymer-filler combinations for TIMs have been explored to maximize the composite thermal conductivity, while only leading to thermal conductivities of up to 2 W m-1K-1. One of the primary limitations to efficient thermal transport in TIMs lies in the boundary resistance generated by the point-contact of filler particles. Additionally, the thermally conductive inclusions are often rigid particles which can lower the elasticity of the composite at high fill factors. Increasing the effective contact area between filler materials could potentially result in much higher composite thermal conductivities [1,2]. Previous work done by Ralphs et al. has shown a substantial increase in thermal conductivity by up to 17 W m-1K-1 with copper particles bridged by liquid metals in a PDMS matrix [3].
In this work, multi-phase fillers comprised of a solid metal core with a liquid metal shell are proposed as a promising solution to reducing point-contact boundary resistance. Liquid metals form a self-limiting oxide layer that encapsulates the liquid metal and can rupture under applied pressure, therefore allowing liquid metal coated particles to connect. Due to the tendency of liquid metal to alloy with and/or embrittle many metals, tungsten is selected as the core material for its relative inertness towards liquid metals. In addition, tungsten particles coated with liquid metals can also be mechanically processed to increase the effective contact area between adjacent particles. The novel combination of deformable liquid shells and highly thermally conductive solid particles can potentially lead to composite materials that facilitate more efficient heat transport and are still stretchable. This research seeks to demonstrate a reduction in thermal boundary resistance that improves TIMs through novel materials processing methods.

References:

QN05.06.22
Nanoscale Thermal Transport in Lithiated Si Anode Films
Azat Abdullaev1, Talgat Yakupov2, Aliya Mukanova1, Assiya Yermekambetova1, Zhumbabay Bakenov1 and Zhandos Utegulov2; 1Department of Chemical Engineering, School of Chemistry, Nazarbayev University, Astana, Kazakhstan; 2Department of Physics, School of Science and Technology, Nazarbayev University, Astana, Kazakhstan.

Rechargeable Li-ion batteries (LIBs) are very promising candidates for electrochemical energy storage in electrical vehichles. Electrical conduction properties in these systems are strongly affected by thermal transport properties during electrochemical cycling. Therefore, thermal management in these systems is very crucial for the control of electrical properties of these storage devices [1]. Si-based anode is a very attractive material because of potentially large achievable capacity of 3700 mAhg−1 [2] that is ten times more than that for graphite carbon, which is mainly used as an anode material in LIBs. However it is well known that Si electrodes suffer from volumetric change during the electrochemical cycling/recycling processes, which in turn leads to change in mechanical and electrical properties. But little research has been done on thermal conductivity variation in Si films during the lithiation. In this work we aim to study nanoscale thermal transport in this nanoscale-thick material using ex situ picosecond time-domain thermoreflectance (TDTTR) approach [3]. RF magnetron sputtering was used to deposit a ~300 nm thick Si films on glass substrate. A 50 nm thick Al was deposited on top of Si serving as an optical absorber and efficient heat transducer in TDTTR experiments. The lithiation of films has been performed in the beaker cell with lithium hexafluorophosphate (LiPF6) in the solution of ethylene, diethyl carbonate and ethyl methyl carbonates (EC:DC:EMC = 1:1:1, v/v) using a constant current of 25 µA up to 0.05 V. Thermal transport measurements were done for non-lithiated and lithiated samples. The results show that for non-lithiated amorphous Si films the thermal conductivity value is ~1.4 W/m*K, which is very close to literature value [4]. After electrochemical lithiation process, the thermal conductivity of lithiated amorphous Si was in the range between 1.3 to 2.2 W/m*K. This sizeable thermal transport fluctuation was likely due to inhomogeneous lateral Li ion distribution on the near-surface region. We also have done measurements on Young’s elastic modulus of these thin film materials using nanosecond laser pulse-induced surface acoustic waves. The results showed the decrease in Young’s modulus after lithiation as it is expected because of volumetric expansion of Si crystal.

Funding from MES RK state-targeted programs BR05236454, BR05236524 and grant AP05130446 is acknowledged.

References:

QN05.06.23
Solid-Solid Phase Change Composite for Thermal Energy Harvesting and Storage
Waseem Afzal1, Talgat Yakupov2, Aliya Mukanova1, Assiya Yermekambetova1, Zhumbabay Bakenov1 and Zhandos Utegulov2; 1Department of Chemical Engineering, School of Chemistry, Nazarbayev University, Astana, Kazakhstan; 2Department of Physics, School of Science and Technology, Nazarbayev University, Astana, Kazakhstan.

The phase change materials (PCMs) provide state-of-the-art thermal energy storage capability and offer enormous potential for the development of sustainable energy infrastructure. However, the widespread utilization of PCMs in real life applications is often limited by the intrinsic material problems including shape instability, structural rigidity, low conductivity as well as the lack of multi-charging modes. Therefore, the functionality of PCMs in order to overcome the aforementioned issues has remained an elusive goal. In current study, we developed nano-pore confined solid-solid phase change composites (PCCs) by infiltrating polyurethane into the pores of carbon nanotube sponge (CNTs). Our fabricated composite structure is dual formable, flexible, highly conductive and more importantly can store thermal energy by mean of low voltage as well as sunlight irradiation, which overcomes the intermittency of input energy source. To the best of our knowledge, we achieved the highest energy conversion efficiencies (94.5 %) for both electro and photo to thermal energy storage among all functionalized PCMs. This high-energy storage efficiency is attributed to the excellent energy conversion/transfer performance of aligned carbon nanotubes (CNTs) network, which remains unaffected over 100 cycles owing to the solid-state phase transition of confined PCM. Moreover, the alignment of CNTs results in anisotropy in thermal transport, which has potential in harvesting/transferring energy in favorable direction. Furthermore, our devised composite with 90 wt% of PCM presents energy storage density 132 J g−1 which is close to solid-liquid PCMs and higher than all the solid-solid PCMs. The combination of multiple features is realized in one single structure, which sets our work apart from previously reported PCCs. Therefore, the presented study will provide breakthrough towards the development of real life applicable PCCs for thermal energy applications.

QN05.06.24
Radiative Cooling Device Design Boosted by Machine Learning
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Due to the major concern on global warming and energy crises issues, radiative cooling devices which utilize the unattapped cold space as potential heat sink, has attracted intense attention again with the newly development in nanotechnology. Many successful experiment results on radiative cooling have focused on blocking the solar energy absorption (0.4−4 µm) and maximizing the thermal radiation loss (~4 µm) to the surrounding simultaneously, which shows exciting temperature drop even under the direct sunshine. However, this design policy may suffer from absorbing too much downward atmospheric radiation in hot and humid regions, thus could be less effective in cooling. Selective emitter which only emit or absorb thermal energy within the 8-13 µm-atmospheric window can tap the most potential of the transparency of atmosphere and get lower stagnation temperature. To our best knowledge, there is no reported work which shows perfect selective emissivity property matching with the atmospheric window.

In this work, we combined the traditional grating and multi-layer structure, aiming to get ideal optical response for radiative cooling purpose. The machine learning optimization was based on Bayesian algorithm and the optical property of the selective coating was calculated by the rigorous coupled wave analysis (RCWA) method. For the design, the ideal optical response property should only have unity emissivity in the 8-13 um wavelength range and unity reflectance outside the transparency window. We employed the typical polar material SiO2 as the grating material on the top to excite the surface phonon polariton. The multi-layer structure consists of Si3N4, Al2O3, SiC and Si with various thickness and sequence was used to manipulate the resonance position. We used silver thin film with sufficient thickness as substrate to totally reflect the solar energy. The periodic length, thickness and filling ratio of the top grating layer, the sequence and thickness of the multilayer structure were optimized by Bayesian and Alex Greaney. We obtain the optimal structure with nearly unity emissivity only in the atmospheric window.

QN05.06.25
Modeling Thermal Resistance Across Contacting Interfaces Including Surface Characteristics
Seshu Nimmala1, Aria Hosseini2, Jackson Harter2, Todd Palmer2, Eric Lenz1 and Alex Greeney1; 1Lam Research Corporation, Tualatin, Oregon, United States; 2University of California, Riverside, Riverside, California, United States; 3Oregon State University, Corvallis, Oregon, United States.

Thermal resistance across the interface between touching surfaces is critical for many industrial applications. Contacting interfaces are fractally rough, with locally intimate contact separated by regions with a wider gas filled boundary gap. Heat flow across the interface is heterogeneous and thus the contact model is based on a network of thermal resistors representing boundary resistance at local contacts and the access resistance for lateral transport to contacts. In a previous work [1], we developed a network model to predict the macroscopic thermal resistance of mechanically contacting surfaces. The results of molecular dynamics simulations to characterize boundary resistance of Silicon Alumina.
interfaces and the Boltzmann transport simulations of access resistance in Si in the ballistic transport regime were presented. In the present work, we review some of the current state-of-the-art and highlight the advanced models developed including surface characteristics such as roughness at interfaces. Additionally, we report some of the results of analyses when the components are subjected to variables such as pressure and temperature. This study is of practical significance in understanding the influence of surface roughness in thermal transport across interfaces at nanoscale to macroscale (i.e., multiscale) for applications such as thin films in the semiconductor industry, and mechanical components in industrial equipment.


**QN05.06.26**
Formation of Three-Dimensional Segregated Network of Nanofillers for Epoxy Composites of High Thermal Conductivity
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The development of the electronic devices towards smaller design, higher power consumption, and multiple functions requires an effective heat dissipation during operation. The self-assembled carbon nanotubes (oCNTs), hexagonal boron nitrides (hBN) and graphene oxide v were prepared to improve the thermal conductivity while maintaining the electrical insulation properties of the epoxy composites. The oCNTs and graphene oxide were separately immobilized on the edges of hexagonal boron nitride, which prevent oCNTs from continuously contacting with each other. The thermal conductivity the hybrid nanofiller/epoxy composites were measured and compared with the bare epoxy. The thermal conductivity of the epoxy composites containing 20 vol% of oCNTs@hBN10 was 1.26 W/m·K, which is higher than 600% compared to that of bare epoxy and the volume resistivity of the epoxy composites was in an insulating region even at high content of nanofiller. The significant improvement in thermal conductivity was attributed to the formation of linkages between oCNTs and hBN and the good compatibility of the hybrid filler in the epoxy matrix. This work was supported by Korea National University of Transportation in 2018.

**QN05.06.27**
Reducing Thermal Conductivity Through Lattice Softening
Riley C. Hanus, G. J. Snyder and Matthias T. Agne; Northwestern University, Chicago, Illinois, United States.

Two fundamentally different avenues for controlling a materials thermal conductivity are phonon scattering and lattice softening. In the phonon scattering picture, the phonon dispersion relation and group velocities are assumed to be fixed and lattice defects reduce lattice thermal conductivity ($\kappa_L$) by introducing phonon scattering centers. Lattice softening recognizes that lattice defects alter the phonon dispersion relation and thus reduce $\kappa_L$ by reducing phonon frequencies and group velocities. Here, I will present experimental data on several systems (Si, PbTe, and SnTe) which demonstrate that microstructural defects such as grain boundaries, dislocations, and vacancies can significantly soften a materials lattice, reducing the materials speed of sound and elastic moduli. By analyzing the data on elasticity and thermal conductivity through standard transport modeling, it is shown that lattice softening is a dominate mechanism for the reduction of $\kappa_L$ in these systems. Additionally, it will be shown that lattice softening is theoretically expected to be more effective than phonon scattering effects in anharmonic materials and at high temperatures. This work demonstrates how lattice softening is emerging as an important mechanism for controlling a materials thermal conductivity, and provides new avenues to engineer a materials $\kappa_L$, beyond phonon scattering.

**QN05.06.28**
Design of Microporous Copper Inverse Opal Wicks for Capillary-Driven Boiling
Chi Zhang1, James W. Palko1,2, Michael Barako1,2, Mehdi Asheghi2, Juan G. Santiago2 and Kenneth Goodson1; 1Stanford University, Stanford, California, United States; 2University of California, Merced, Merced, California, United States; "NG Next Basic Research Laboratory, Redondo Beach, California, United States.

Rising power densities have presented thermal management challenges to a number of industrial applications such as power electronics, laser diodes, microprocessors, and defense and space systems. These high-performance devices, however, can generate hotspots with extreme heat fluxes (exceeding 500 W cm$^{-2}$) within a small area (typically submillimeter by submillimeter), leading to local temperature spikes. Accordingly, significant research attention has focused on efficient heat dissipation from local hotspots to reduce device temperature and ensure performance and system reliability. Liquid to vapor phase-change process provides an attractive approach for hotspot thermal management by utilizing the latent heat of working fluid during vaporization.

Microporous metals are promising for applications that require simultaneous transport of fluid through the pore space and heat conduction through the matrix to a surface where they interact. They are common as wick structures in two-phase thermal management systems such as vapor chambers and micro heat pipes due to their potential to reduce the transport resistance associated with the heat supply, liquid replenishing, and vapor removal. Passive microporous structures depend on capillary pressure to supply liquid to the phase-change surface where the working fluid evaporates. The low thermal resistance characteristics of such two-phase operating mechanisms are enabled by the latent heat exchange at nearly constant evaporator temperatures. Inverse opals (IO) are ordered porous media that consist of uniform pores arranged periodically to form a fluid permeable structure. The regular order of these porous structures makes it feasible to accurately predict the fluid transport property using single unit cell analyses and also to fine tune the structural features such as pore diameter and porosity.

We experimentally characterize capillary-driven boiling in well-defined copper inverse opal wicks that consist of uniform pores with diameter ranging from 3 $\mu$m to 10 $\mu$m. Template sintering is utilized to improve the IO permeability by over an order of magnitude, leading to a concomitant increase in boiling critical heat fluxes (CHF). Liquid wicking distances and capillary wick thicknesses are also systematically varied to investigate their effect on the CHF. A semi-analytical model is developed to account for both liquid and vapor transport within the microporous wicks, which predicts the CHF with ±30% accuracy compared to our experimental data. Understanding the characteristics of boiling process in capillary wicking structures is essential to wick design optimization in high-performance vapor chambers, thermal ground planes, and other two-phase heat spreaders.

**QN05.06.29**
Role of Gallium Oxide on Thermal Performance of Liquid Metal Droplet Based Thermal Interface Materials
Matthew Ralphs, Wilson Kong, Robert Wang and Konrad Rykaczewski; Arizona State University, Tempe, Arizona, United States.

Gallium-based room temperature liquid metals have become a hot topic in the thermal management of traditional semiconductor packaging and stretchable electronics. However, the native gallium oxide shell on these liquids both facilitates many unique processing techniques as well as hinders others, making it a force that needs to be reckoned with. Some studies have been done on chemically and mechanically altering the oxide layer, but very few have focused on the thermal ramifications of the oxide and its rupture. In this work, we present a comprehensive set of experiments on parameters controlling fracturing of the oxide shell on micro and nanoscale liquid metal droplets and the resulting thermal conductivity of the droplet ensemble. Specifically, we fabricate liquid metal droplets with diameters ranging from hundreds of nanometers to ten micrometers and pack them into macroscopic films. We then compress the films while measuring thermal resistance, pressure, and electrical resistance in situ through and beyond oxide rupture. This allows us to interrogate the mechanical role of the oxide layer and the thermal ramifications of the oxide shells when dealing with liquid metal droplets. Various sizes of liquid metal droplets are investigated as well as mixtures of liquid metal droplets and solid metal particles. The inclusion of solid and liquid metal particles together gives insight into the role of particle packing and how it relates to thermal resistance and oxide failure. The measured thermal properties and how they relate to the mechanics of the rupturing oxide will be explained. Additionally, this work will lead to insights on using liquid metal coated solid metal particles in a polymer composite to reduce the thermal boundary resistance between particles and greatly enhance the thermal conductivity of such composites.

**QN05.06.30**
Modeling of a Water-Harvesting Thermal Battery with a NIPAAm Hydrogel Sorbent
Jordan Kocher, Yanan Zhang and Robert Wang; Arizona State University, Tempe, Arizona, United States.

Thermal energy storage devices (i.e., “thermal batteries”) are utilized in scenarios where thermal energy is available at certain times but required for use at a later time. The amount of energy that can be stored within a thermal energy storage device depends on both the storage material and the mode of storage. Systems that incorporate thermochemical processes are often able to store significantly more energy than sensible and latent heat thermal energy storage systems.
This presentation focuses on the use of N-isopropylacrylamide (NIPAAm) for sorption thermal energy storage. NIPAAm is a thermoresponsive polymer that transitions from hydrophilic to hydrophobic upon crossing its critical temperature (typically 32 °C). In addition, NIPAAm has the ability to absorb water vapor (i.e. humidity) and expel liquid water. This creates huge energy savings potential during sorbent regeneration that is equivalent to the enthalpy of vaporization of water. The energy density of NIPAAm is also particularly attractive because it can be used in conjunction with hydrogels that can store up to 40 times the gel's dehydrated mass in water.

To explore the potential of NIPAAm for cooling applications, we conduct system-level modeling of sorption systems utilizing this novel material. This system charges up by absorbing water from humid air that is passed through the device. When cooling is desired, the NIPAAm is heated above to 32 °C to expel liquid water that is then evaporated to cool the system. This sorption process can potentially exceed the energy density of traditional latent heat systems (e.g. cold thermal storage with ice) because the enthalpy of vaporization significantly exceeds the enthalpy of melting. The presentation on sorption system modeling with NIPAAm will highlight the exciting opportunities for this novel material in thermal energy storage applications.

QN05.06.31
**Advanced Building-Envelope Component Materials for Optimal Energy Retrofiting Measures of Office Building Façades**

Abantika Sengupta1 and Tivasa Ray1; 1Arizona State University, Tempe, Arizona, United States; 2Politecnico di Milano, Milano, Italy.

Built environment accounts for most of the overall life cycle energy consumption and greenhouse gas emissions. Buildings are a major source of global energy demand and materials, that in return produces large carbon footprint and GHG (Green House Gases) as the by-product. The 2030 Carbon emission reduction challenge sets aggressive goals for slowing down the growth rate of GHG and reducing the Carbon Footprint of the buildings to address climate change. A major sustainable challenge for the buildings is to be resilient during their Life Cycle, for which they need maintenance from time to time within this period to prevent their performance degradation. The building should perform in terms of functionality and energy demands. Buildings which do not meet the energy standards require extensive renovation including façade retrofit, to meet the energy performance and carbon reduction goals for the future. As a reasonable retrofit of the façade, materials play a very important role. With the advancement in material technology and the use of smart materials connected to the building automation systems, zero energy or minimizing the energy demand of the buildings are in trends. Usage of smart or advanced materials should also be weighed with the initial cost, environmental impact, market value, life cycle analysis, maintenance cost along with the sustainable use of local materials. The significance of retrofitting of building façades lies not only in enhancing the energy efficiency or energy-based models but also in the creation of construction markets and business models. Creating value and value proposition for the building retrofit are key to encourage more buildings to adopt this kind of method. Retrofit and refurbishment systems create possibilities to add value to the customers outside the economic area and reduce energy consumption. This creates co-benefits. The major significance of retrofitting of the existing building lies in the analysis of cost reduction incurred as compared to a newly built structure. Abatement in systems cost can also be achieved from attrition of wastage of materials and surplus materials control. Since buildings consume a significant amount of energy (40 per cent of the nation's total U.S. energy consumption) and the existing ones comprise the largest segment of the built environment, retrofitting offers significant opportunities in terms of customization according to the climate, orientation and typology of the building and energy efficiency improvement. Hence sustainability can be achieved in this sector at lower costs and higher uptake rates. The article will propose retrofitting of the façade system of an office building in Giosa, Milan, Italy, additionally adding a static shading element. The study focuses on the diverse façade system and the typology of shading elements for each of them along with the materials used. Apart from energy conservation, retrofitting the existing office building also yields to the key design objectives which include illumination and daylight factor analysis and impact of the façade components on the structural system. This project emphasizes especially on the thermal analysis of the façade system-thermal bridges, water and air permeability, resistance against impact and fire resistivity of the materials in use. Use of advanced materials, its impact on the environment and the analysis of the energy consumption and energy savings form the framework for the retrofit project along with the goal of carbon footprint reduction.

QN05.06.32
**Design and Optimization of the Advanced Silica Nanofiber Insulator Material Properties via Coarse-Grain Molecular Dynamics Simulation Method**

Gorakh Pawar, Bjorn Vaegensmith and Tamnie Borders; Idaho National Laboratory, Idaho Falls, Idaho, United States.

The role of the computational material modeling and simulations is indispensable in the design and development of advanced materials with superior material properties. Here we present a coarse-grained molecular dynamics (CGMD) simulations-based investigation to understand a melting behavior of the mesoscopic electro-spon silica-nanofiber based insulator materials, and subsequently elucidate the silica nanofiber size-melting temperature relationship. A coarse-grained bead, which is equivalent to the spherical (SiO2)6 silica atomic structure, was used to construct the several mesoscopic silica nanofiber structures with sizes \( \sim 100 \text{ nm} \) that were consequently simulated for several hundred nanoseconds. The temporal bead trajectory information was used to decipher the melting behavior of the silica nanofibers. The silica nanofiber size-melting temperature dependency evaluated through CGMD simulations could provide some valuable guidelines for the further optimization of the silica nanofiber manufacturing processes.

QN05.06.33
**Energy Conversion Using Ferroelectric Properties of Barium Titanate**

Mariana Verdugo1, 2, Ashley Bucsek3, William Nun3, 2, Bharat Jalan2 and Richard D. James2; 1University of California, Berkeley, Berkeley, California, United States; 2University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

In the United States, nearly 68% of the primary energy produced each year is wasted as heat. A couple tangible examples of this wasted energy is the heat that radiates from laptops and air conditioning units that remove heat from air and release it into the environment. It would be efficient to convert this waste heat into a better source of energy such as current. Using the ferroelectric properties of BaTiO3, this energy conversion can be done.

BaTiO3 undergoes structural transitions when heat is applied at its curie temperature, approximately 120-130°C. During this structural transition, BaTiO3 goes from paraelectric to ferroelectric. While in its ferroelectric state, BaTiO3 behaves like a very good capacitor and during its paraelectric state, it behaves like a poor capacitor. Consequently, we can attach BaTiO3 to a circuit with a reference capacitor (ordinary capacitor), and we can charge this circuit to equilibrium and remove all energy sources. As BaTiO3 is heated and cooled, current flows from the reference capacitor to the activate BaTiO3 capacitor. Experimentally, we have observed the current flows consistently as the heat oscillates in the curie temperature range.

Converting waste heat to current is an efficient energy conversion method.

QN05.06.34
**Effects of Chemical Intercalation, Strain and Phase Transition on Thermal Transport in Bulk and Single-Layer MoS2**

Shanla Chen1, Aditya Sood3, Bin Ouyang2, Shinbyoung Xuong1, Eric Pop3, Kenneth Goodson2 and Davide Donadio1; 1University of California Davis, Davis, California, United States; 2Stanford University, Standford, California, United States; 3University of California, Berkeley, Berkeley, California, United States; 4Soochow University, Suzhou, China.

The possibility of tuning the vibrational properties and the thermal conductivity of layered van der Waals materials either chemically or mechanically would open a way to significant advances in nanoscale heat management, which is of importance for potential applications in energy storage, nanoelectronics and optoelectronics. Here we investigate the effects of lithium intercalation, cross-plane strain and phase transition on thermal transport in bulk and single-layer MoS2, by first principles calculations. Our well converged, parameter-free calculations resolve discrepancies in the literature about the thermal conductivity of MoS2, predict the strong modulation effects by mechanical strain, lithium intercalation and phase transition, and provide a detailed microscopic interpretation of recent experiments and benchmarks for future ones. Our findings can be exploited to design novel phononic devices, as well as for thermal management in MoS2-based electronics and optoelectronic systems.

QN05.06.35
**Magnetothermal Transport Behavior in Ferromagnetic and Semiconductor Thin Films**

Anand Kataliha1, Ravindra G. Bhardwaj1 and Sandeep Kumar2; 1Department of Mechanical Engineering, University of California, Riverside, California, United States; 2Materials Science and Engineering Program, University of California, Riverside, California, United States.
In this work, we present an experimental study on magneto-thermal transport and spin-Seebeck effect behavior in ferromagnetic and semiconductor materials. The magneto-thermal transport measurements are carried out using in-plane self-heating three-omega method. The in-plane three-omega measurement requires a freestanding specimen. We address this challenge using micro-electro-mechanical systems (MEMS) fabrication methods. The measurements are carried out on Py/Au and Py/Si. We also demonstrate giant spin-Seebeck effect in Py/Si bilayer thin films. The magneto-thermal transport measurements on these thin films are essential for the design and development of energy efficient spintronics devices. We employ four point probe configuration for our MEMS device structure to probe mainly the second and third harmonic voltages as well as resistance with respect to changing temperature and applied magnetic field. The results can be related to thermal transport properties of the system using the three-omega method as mentioned above.

**QN05.06.36**

**Quasi-Ballistic Thermal Transport in Amorphous Silicon Using Transient Grating Spectroscopy**

*Taeyong Kim, Jaeyun Moon and Austin J. Minnich; California Institute of Technology, Pasadena, California, United States.*

Disordered media are of special interest due to low thermal conductivity. Amorphous silicon (a-Si) has been widely used due to their low-cost potential. Due to the lack of long-range order, identifying thermal transport in amorphous media has been challenging. For example, mean-free paths (MFPs) distribution of propagon, a propagating delocalized atomic vibrational state, and its contribution to the thermal conductivity have long been contentious. Here, we report measurements of in-plane quasi-ballistic thermal transport from 30 K to 300 K on a 10 μm length for the measured film. The measurements are carried out using in-plane self-heating three-omega method. The in-plane three-omega measurement requires a freestanding specimen. We address this challenge using micro-electro-mechanical systems (MEMS) fabrication methods. The measurements are carried out on Py/Au and Py/Si. We also demonstrate giant spin-Seebeck effect in Py/Si bilayer thin films. The magneto-thermal transport measurements on these thin films are essential for the design and development of energy efficient spintronics devices. We employ four point probe configuration for our MEMS device structure to probe mainly the second and third harmonic voltages as well as resistance with respect to changing temperature and applied magnetic field. The results can be related to thermal transport properties of the system using the three-omega method as mentioned above.

**Reference:**


**QN05.06.37**

**Investigation on Thermal Conductivity of BAs Monolayer—A First-Principles Study**

*Zhongyang Wang, Lei Liu, Rui Dai, Qiong Nian, Houlong Zhuang and Robert Wang; 1Arizona State University, Tempe, Arizona, United States.*

Cubic boron arsenide (BAs) bulk crystal has been identified to have an ultrahigh thermal conductivity (~1300 Wm⁻¹K⁻¹) both theoretically and experimentally. On the other hand, two-dimensional (2D) stable monolayers of BAs have also been reported to have promising electronic, transport, optical and thermoelectric properties. However, the thermal conductivity of BAs monolayers has not yet been investigated. Does thermal transport in BAs monolayers parallel that of cubic BAs bulk crystals? We present our first-principles study on the thermal conductivity of BAs monolayers.

The vibrational spectra of BAs monolayers have been calculated and are quite different from that of cubic BAs bulk crystals. Two transversal acoustic and optical branches, which correspond to out-of-plane atomic vibrations in BAs monolayers, carry lower energy due to the fact that atoms can more easily vibrate perpendicularly to the plane. The so-called “acoustic bunching” behavior in cubic BAs is also not seen in the vibrational spectra of BAs monolayer due to the presence of these out-of-plane branches. Nonetheless, the giant phononic band gap between the two in-plane optical branches still exists in the vibrational spectra of BAs monolayers. At this point, qualitative analysis of thermal transport based on the vibration spectra is inconclusive. More rigorous computational techniques need to be performed to derive the lattice thermal conductivity of BAs monolayers.

For our computations, we employ density-functional perturbation theory to generate second-order (harmonic) and third-order (anharmonic) interatomic force constants (IFC) for BAs monolayer using the VASP package. The harmonic IFC allows us to derive the vibrational properties, while the anharmonic IFC allows us to determine the three-phonon scattering rates using Fermi’s golden rule. With the only inputs of harmonic and anharmonic IFC, we can derive the lattice thermal conductivity by solving the exact phonon Boltzmann Transport Equation using the ShengBTE package.

**Reference:**


**QN05.06.38**

**Thermal Conductivity Mapping of High-Entropy Carbides and Diborides**

*Jeffrey Braun, 1David Olson, 2Joshua Gild, 3Tyler Harrington, 4Jian Luo, 2Kenneth Vecchio and 2Patrick Hopkins; 1University of Virginia, Charlottesville, Virginia, United States; 2Materials Science and Engineering, University of California, San Diego, La Jolla, California, United States.*

In aerospace applications operating at very high temperatures (>3000 K), such as hypersonic flight or rocket propulsion systems, there is a critical need for the development of materials which can survive such extreme temperatures. To meet this need, ultra-high temperature ceramics (UHTCs) have proven to be at the forefront of research. While early development of UHTCs were primarily focused on SiC and Si₃N₄ currently there is a strong interest in transition metal diborides such as hafnium diboride (HfB₂) and zirconium diboride (ZrB₂) as well as carbides such as hafnium carbide (HfC) and tantalum carbide (TaC). Looking beyond binary carbides and diborides, materials synthesis of high-entropy ceramics consisting of five or more elements has enabled a new research direction to explore the engineering of thermophysical properties to enable sustainable high-temperature applications.

One of the most critical properties to understand in these systems is thermal conductivity. Nearly temperature independent diffusivity further shows that anharmonic scattering may not be dominant over the temperature range that we studied: 30 (K) to 300 (K). Our non-contact measurement will provide useful insights into studying disordered materials that have been challenging with conventional thermal characterization methods.

**Reference:**


**QN05.06.39**

**Measuring Ballistic Thermal Resistance within a Nanoslot-Patterned Si Thin Film**

*Dongchao Xu, Yue Xiao, Fabian Medina, Qiyu Chen and Qing Hao; University of Arizona, Tucson, Arizona, United States.*

Phonon transport within nanosporous materials has been widely studied for its potential applications in thermoelectrics, heat waveguides, thermal diodes, and heat imaging. As an alternative to the conventional nanoporous structures, graphene with a patterned row of periodic nanoslots has been proposed for its potential application in tuning the thermal conductivity [1]. Here we report the narrow channel between two adjacent nanoslots functions as a nanoconstriction to restrict the phonon transport. Phonons will transport ballistically through the channel if the phonon mean free paths (MFPs) are much longer than the neck width, subsequently creating a “ballistic thermal resistance” to restrict heat conduction. Some earlier analytical studies on ballistic thermal resistances have been carried out on a heated nanoparticle inside a host medium [2], and nanostructures on a planar substrate [3]. The ballistic thermal resistances have been experimentally observed between nanosized heaters and a substrate [4].

In this work, the ballistic thermal resistance introduced by patterned nanoslots on a Si thin film is systematically studied. With ~10 μm length for the measured film, a single neck of 50 to 200 nm width is fabricated in the middle of the film. Compared with phonon transmission studies across nanoslots patterned on a 1-μm-long bridge between two suspended membranes [5], our measured films can incorporate the thermal conductivity contribution from phonons with much longer MFPs, which becomes more critical at cryogenic temperatures. The measurement results are further compared to predictions by frequency-dependent phonon Monte Carlo simulations. Our technique provides a simple way to justify the ballistic thermal resistance for various film- or flake-like materials.
Our recent experimental study in developing boron arsenide and boron phosphide has led to the synthesis of high quality materials and the observation of ultrahigh thermal conductivity of 3800 W/mK and 500 W/mK respectively. However, when integrated to electronic devices, further investigation is needed to understand thermal transport at multiscales and interfaces. Here we developed multiscale modeling to capture thermal transport from diffusive to ballistic transport and across the high thermal conductivity boron compound interfaces. We derive the interatomic force constants from density functional theory calculations and extract thermal conductivity by solving the steady state Boltzmann transport equation with full collision term beyond relaxation time approximation. We performed a multiscale simulation by solving the time-dependent three-dimensional spectral phonon Boltzmann equation using variance-reduced Monte Carlo method. We proposed a new theory to quantify interfacial phonon transport and the temperature evolution near interface. Our ab initio calculations demonstrate very good consistency with experimental measurements. This study systematically investigated the thermal transport of the newly developed emerging high thermal conductivity boron compounds at varied sizes and near interface. Our development paves the pathway towards establishing the system-level design of advanced thermal management of high-power electronics using these emerging high thermal conductivity semiconductors.


Experimental Study of Solar Thermophotovoltaic Energy Conversion Enhanced with Selective Metalfilm Coatings

Ryan McBurney, Qing Ni and Leping Wang; Arizona State University, Tempe, Arizona, United States.

Theoretical studies have shown that solar thermophotovoltaic (STPV) systems have the potential to produce efficiencies up to 85\%, but current technology has only reported actual efficiencies around 6.8\%. Studies have clearly shown that the major drawbacks in the components of a STPV system are the solar absorber and emitter. Current solar absorbers have shown to have high thermal emission causing heat loss and emitters display a lack in thermal emission above the bandgap of TPV cells. It is desired to have a solar absorber with unit absorbance in the solar spectrum, while having zero emittance in the longer wavelengths. In addition to this, emitters need to have unity emittance only within a narrow band that matches the high quantum efficiency of a specific TPV cell to minimize non-useful photons. Our experimental study will mainly address the issue of high thermal emission of solar absorbers by applying the highly-efficient selective metalfilm coating recently developed in our lab. We propose to use the metalfilm which has demonstrated high temperature thermal stability, as a solar absorber to investigate STPV system energy conversion. We will also address the potential to use such selective coatings as a selective emitter with further structure optimization to further improve STPV systems. The result of our experimental study will produce a better understanding of loss mechanism in STPV systems and bridge the gap between theoretical studies and real application. Our theoretical calculations predict a potential to achieve an STPV efficiency of 10\% or higher with the aforementioned metalfilm selective solar absorber and TPV emitter. In conclusion, this project, by closely examining the inefficiencies of solar absorbers in STPV systems, will bring to light the potential of highly-selective metalfilm enhanced STPV systems.

In Situ Thermal-Mechanical Diagnostics and Extreme-Condition Transport for Battery Thermal Management

Huuduy Nguyen, Ming Ke, Albert Rieck, Joon Sang Kang and Yongjie Hu; University of California, Los Angeles, Los Angeles, California, United States.

Thermal management has become critically important for today's batteries due to safety issues under increasing power and energy density. A clear and straightforward in-situ diagnostic method during the device normal operation process is highly desirable and can elaborate the fundamental materials dynamics for superior performance. We will describe our recent work on the first time demonstration of in situ thermal-electrochemical characterization in a lithium ion battery. We developed a novel approach that integrates ultrafast optical spectroscopy and electrochemical control to investigate the thermal transport in the electrode materials during the battery's normal operation process. The study reveals intriguing anisotropicphonon interactions and highly reversible electrochemical control over the thermal properties. In addition, we investigated state-of-charge dependent ion diffusivity of electrode at the organic-inorganic interfaces and observed significant improvement in ion diffusivity through microscopic structural optimization. Moreover, we explored phase change material for battery temperature control and showed substantial reduction in peak temperature that prevents thermal runaway at extreme conditions. The impact of this study to rational design and improve thermal management of lithium ion batteries working at extreme conditions will also be discussed.

References:

Metasurface Filter Made of Plasmonic Nanodisk Array for Enhancing Thermophotovoltaic Energy Conversion

Rajagopalan Ramesh, Qing Ni, Hassan Alshehri and Leping Wang; Arizona State University, Tempe, Arizona, United States.

A basic thermophotovoltaic (TPV) system consists of a thermal emitter and a photovoltaic cell that converts heat to electricity via infrared photons or thermal radiation. While great progress has been reported recently to achieve spectrally-selective thermal emitters made of photonic crystals, metamaterials and multilayers, a wavelength selective optical filter is another possible route to increase the TPV efficiency by reflecting the photons with energy below the bandgap at longer wavelengths. Optical filters with narrow transmission band right above the bandgap of TPV cells are not restrained by the rigorous thermal reliability as required for the emitters. In this work, we fabricate and characterize a novel metasurface filter made of an aluminum (Al) nanodisc array to achieve spectrally selective transmission above the bandgap of TPV cell. The filter is fabricated by depositing thin Al onto the quartz substrate which is covered by anodized aluminum oxide (AAO) templates. Optical simulations will be carefully performed to determine the appropriate AAO interpore distance, AAO pore diameter and the Al film thickness such that the resulting Al nanodisc array will show narrowband transmission at a wavelength of 1.6 micron, which is the bandgap of a commercial Gallium Antimonide (GaSb) TPV cell. Preliminary simulations indicate that the narrow-band transmission is due to the articular magnetic resonance between neighboring Al nanodiscs, which channels energy through at wavelengths near the resonance. The optical and radiative properties of the Al nanodisc metasurfaces will be characterized by an FTIR spectrometer and a monochromator with an integrating sphere. The external quantum efficiency (EQE) of the commercial GaSb TPV cell will be measured with and without the fabricated metasurface filter covered, aiming to show the narrow-band EQE spectrum right above the cell bandgap due to the spectral filtering. By pairing the filter with a tungsten thin film emitter at 600\°C or higher, the I-V curve from the GaSb TPV cell will be measured and the heat-to-power TPV efficiency will be calculated. Enhanced TPV efficiency is sought to be experimentally demonstrated with the metasurface filter. Theoretical energy analysis for the TPV system will be performed to validate and explain the experimental data.
Regulating Near-Field Radiative Heat Transfer with Tunable Materials

Liping Wang, Xiaoyan Ying and Sydney Taylor; Arizona State University, Tempe, Arizona, United States.

Thermal regulation in solid-state devices has received extensive attention over the years due to its potential applications in thermal management, thermal circuits and thermal computing. Near-field thermal radiation with super-Planckian heat flux beyond Blackbody limit inspired a new route for thermal control with thermal photons, particularly with recent achievements in near-field radiative heat transfer measurements. In this talk, we will first review the theoretical studies on tunable near-field thermal radiation, in particular from our group, such as near-field thermal rectification, thermal switching and thermal modulation based on thermochromic VO₂ and tunable graphene. VO₂, which changes phase between an insulator with strong infrared phonons and a metal with optical phonons around 68degC. Therefore, the near-field coupling due to surface phonon polaritons between VO₂ and another dielectric could be weakened by changing the VO₂ to metallic phase at higher temperatures. As a result, the near-field radiative heat flux can be tuned thermally with the VO₂ temperature. On the other hand, graphene plasmon and its radiative properties can be modulated by chemical doping or electrical gating, such that the near-field coupling strength and resulting radiative heat transfer between graphene surface plasmons can be tuned dynamically. Fabrication and characterization of VO₂ thin films and graphene will be then discussed in detail. By using a plate-plate thermal metrology with nanometer gaps created by sparse polymer posts, we experimentally demonstrate near-field radiative thermal regulation between graphene covered SiO₂/Si plates with 1cm² area for the first time by modulating graphene conductivity through external gating potential. Besides, a near-field radiative thermal rectifier and switch based on VO₂ phase change will be experimentally demonstrated as well. Our work will facilitate the active control of...
near-field thermal radiation in solid-state applications.

8:15 AM QN05.07.02
Electron-Phonon Coupling and Dimensional Crossover in Quasi-1D van der Waals Crystal NbSe$_2$ Nanowires
Lin Yang, Yang Zhao, Qian Zhang and Deyu Li; Vanderbilt University, Nashville, Tennessee, United States.

During the last two decades, tremendous progress has been made in quantitative understanding of several major phonon scattering mechanisms, including phonon-phonon, phonon-boundary, phonon-defects, as they are the determinant factors in lattice thermal transport that is critical for the proper functioning of various electronic and energy conversion devices. However, the roles of another major scattering mechanism, electron-phonon (e-ph) interactions, remain elusive. This is largely due to the lack of solid experimental data for the effects of e-ph scattering in the lattice thermal conductivity for the material systems studied thus far. Through systematic measurements, we show distinct signatures in the lattice thermal conductivity observed below the charge density wave (CDW) transition temperatures in NbSe$_2$ nanowires, a type of quasi-1D van der Waals (vdW) crystals with covalently bonded molecular chains assembled together through vdW interactions. Owing to the restricted dimensionality, the density of free electrons in NbSe$_2$ spontaneously develops a wave-like variation due to CDW phase transitions. The variation of charge carrier concentration upon the onset of CDW modulates the e-ph scattering strength, resulting in unique features in the lattice thermal conductivity.

In addition, while the measured lattice thermal conductivity demonstrates a decreasing trend as size reduces for wires with diameter $>$26 nm, an unexpected increasing trend was observed as the lateral dimension further reduces. In fact, the room-temperature thermal conductivity of NbSe$_2$ nanowires could be enhanced by more than 20 fold as the diameter reduces, which is attributed to the dimensional crossover from 3D to 1D for phonon transport in thin NbSe$_2$ nanowires. The excised 1D phonons propagate along the molecular chains and contribute to the observed much enhanced thermal conductivity. These studies provide new insights into thermal transport through vdW crystals, which helps to lay the physical foundation of quasi-1D vdW materials in engineering applications.

8:30 AM QN05.07.03
Role of Anharmonicity in Enhancing Interfacial Thermal Conductance by a Bridging Layer
Jingjie Zhang$^1$, Rouzbeh Rastgarkashgorkolaei$^1$, Carlos Polanco$^2$, Nam Q. Le$^3$, Pamela M. Norris$^1$ and Avik W. Ghosh$^1$; 1University of Virginia, Charlottesville, Virginia, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 3JHU Applied Physics Laboratory, Laurel, Maryland, United States.

A bridging layer with matching properties can facilitate phonon transport across interfaces. In this work, we study the role of anharmonicity in such systems. Our results demonstrate the existence of a minimum interfacial thermal conductance $G$ versus layer thickness $L$ with weak anharmonicity and the existence of a maximum $G$ vs. $L$ with strong anharmonicity. The minimum thermal conductance appears at a thin thickness and is due to the competing roles of quantum effect and anharmonicity. The maximum thermal conductance is a result of two contradictory effects of anharmonicity: “re-thermalization” and “umklapp scattering”. Moreover, we present that the effect of anharmonicity on the conductance can be tuned by varying temperature or bridging layer thickness, as both parameters can change the strength of anharmonicity. Additionally, we propose a critical length $\lambda_s$ as a criteria at which the resistance can be separated as resistances in series in the presence of both weak and strong anharmonicity. Additionally, we compared them to the bulk mean free path $\lambda_b$ and demonstrated that $\lambda_s$ is much smaller than $\lambda_b$, hinting that the summation over resistance rule can be used at much smaller length than the bulk mean free path, and a comparison between $\lambda_s$ with L cannot be used to treat boundary resistance or classical size effect for thin films between two materials.

8:45 AM QN05.07.04
Thermal Materials and Science in Wearable Applications
Yi Cui$^{1,2}$; 1Department of Materials Science and Engineering, Stanford University, Stanford, California, United States; 2Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Wearable applications with multi-function integration afford exciting research opportunities. Among all the functions, effectively regulating the heat flow between human body and environment not only increases thermal comfort but also presents a novel and cost-effective approach for reducing the building energy consumption. Here I will present my group work on thermal consideration and materials design for new generation of textile and wearables. Particularly with regulation of human body infrared radiation, we demonstrated the best heating and cooling textiles. We also develop new concept of bifunctional textile which can switch between heating and cooling mode. In addition, we also demonstrate the cooling textile under the sun.

9:15 AM QN05.07.05
Engineering Thermal Conductivity Through Microstructure
Riley C. Hanus and G. J. Snyder; Northwestern University, Evanston, Illinois, United States.

The flow of heat through materials is a topic of scientific interest and technological importance in fields of microelectronics, power generation, heat management, and thermoelectrics. For example, advancement in microelectronic technologies (e.g. microprocessors, and high-power electronics) demands even more efficient removal of the heat generated in these devices. In contrast, technologies such as thermal barrier coatings and thermoelectric materials are designed to stop the flow of heat. Thus, progress in these fields and many others relies on understanding how microstructural defects such as interfaces, dislocations, and point defects influence a materials thermal conductivity.

In this presentation, I will highlight several experimental and theoretical results which aim to establish a fundamental understanding of heat transport in defective materials. First, I will discuss several studies related to heat conduction across interfaces. Secondly, I will demonstrate in several material systems how defects can soften a materials lattice which reduces the phonon group velocity and thus decreases thermal conductivity. Lattice softening is a fundamentally different avenue to engineer thermal conductivity than phonon-defect scattering. I will then explain why lattice softening is theoretically more effective in anharmonic materials and at high temperatures, and how this is a dominate mechanism at play in several high thermoelectric efficiency (zT>2) PbTe based materials. Finally, I will discuss heat conduction in the ‘fully defective’ or amorphous limit. In this case the lack of sufficient periodicity leads to the concept of a minimum thermal conductivity defined by diffusionasquasiparticles instead of phonons.

9:45 AM BREAK

SESSION QN05.08: Novel Thermal Functionalities in Materials
Session Chairs: Yongjie Hu, Yee Kan Koh, Lucas Lindsay and Amy Marconnet
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 124 B

10:15 AM QN05.08.01
Conveyor-Belt Entropy Transport In Weyl Semimetals—A New Concept for All-Solid-State Heat Switches
Joseph P. Heremans$^1$, Dung Vu$^1$, Nandini Trivedi$^1$, Michael Flatté$^2$ and Cuneyt Sahin$^2$; 1The Ohio State University, Columbus, Ohio, United States; 2The University of Iowa, Iowa City, Iowa, United States.

If they existed, solid-state switches with a large switching ratio between their off and on states would have many applications [1]. They would be particularly useful in combination with magnetocaloric engines and adiabatic demagnetization coolers, which are capable of reaching temperatures of 1 to 100 mK. In this talk, a new physical mechanism will be described for magnetically controlled entropy and heat transport based on the topological properties of Weyl semimetals [2]. Weyl semimetals are electrically conducting solids in which the bulk band structure consists of Dirac bands that come in pairs, with the Dirac points of each pair separated by a wavevector $k$. When the Fermi energy is at the Dirac points, charge is carried in the bulk by both electrons and holes. The carriers also have a Berry curvature $\Omega$. The surface states that correspond to this dispersion have themselves a dispersion that forms an arc in k-space, one on each of the top and bottom surfaces. An applied magnetic field normal to these arcs accelerates the carriers and holes, giving rise to a conveyor-belt flow of particles between the top surface, the bulk, the bottom surface, and the bulk again to the top surface. No net charge current flows since the carriers are of equal density and opposite polarity. Thermal transport along this conveyor belt stands in strong contrast to electrical transport. We show how
in the presence of a temperature gradient, these electrons and holes carry a non-zero entropy along the conveyer belt. This leads to an additional field-driven electronic thermal transport through the vdW cross contact between individual copper phthalocyanine (CuPc) nanoribbons. We establish a brand new perspective that neither RUMs nor phonons with negative Gr"uneisen parameters are necessary (or sufficient) in order for a material to undergo NTE. We elucidate the microscopic fundamental driving mechanisms behind NTE remain largely unknown for all but a handful of systems. One mechanism often invoked to explain NTE in inorganic framework materials and was characterized by its thermal conductance and response time. The switching ratio was calculated from the effective conductance between top and bottom surfaces. Experimental data will be shown on semiconducting Bi-Sb alloys, in which band inversion and a Weyl semimetallic state is induced by Zeeman splitting of the Landau levels. The field-induced thermal conductance dominates the electronic thermal conductivity in longitudinal magnetic fields. The effect is macroscopic and visible on millimeter-sized samples up to 200 K.

10:45 AM QN05.08.02
Two-Channel Thermal Transport in Ordered-Disordered Superionic Ag$_2$Te and Its Traditionally Contradictory Enhancement by Nanotwin Boundary Ming Hu; University of South Carolina, Columbia, South Carolina, United States.

Recent experiment has proved that superionic Ag$_2$Te can achieve a figure of merit as high as 1.39 due to its extremely low thermal conductivity. However, the traditional lattice vibration concept, i.e., phonons regarded as heat carriers, fails to explain the governing mechanism in such structures where anions vibrate around their equilibrium positions while cations flow like a liquid. As a result, the underlying physics for thermal transport properties in superionic Ag$_2$Te is still a mystery. In this study, two-channel heat transport in such ordered–disordered systems (i.e., lattice vibrations and liquid-like mobile ions coexist) is quantitatively characterized on the basis of the heat flux linear response theory. Our results show that the convective thermal conductivity is dominant in the system, which results from the free movement of Ag ions. As a consequence, the total thermal conductivity increases abnormally with temperature due to the strengthened cations’ mobilities at elevated temperatures. Meanwhile, the effect of experimentally observed nanotwin boundaries, which facilitate electrical transport in crystals, on heat carriers are also investigated. In contradiction to the classical heat transport theory, in which heat carriers are hindered by boundaries, the nanotwin boundary in superionic Ag$_2$Te unexpectedly improves thermal transport due to the enhanced movement of Ag ions around the grain boundary. This exhaustive explanation of thermal transport properties in superionic Ag$_2$Te will support the future design of superionic conductors based on thermoelectrics and more broad energy systems composed of ordered–disordered materials.

11:00 AM QN05.08.03
Giant Caloric Effects in Fast-Ion Conductors—A Promising Route for Ambient Solid-State Cooling Claudio Cazorla; The University of New South Wales, Sydney, New South Wales, Australia.

Solid-state cooling is a sustainable and energy efficient refrigerant technology that exploits field-induced reversible transformations in materials. Solid-state cooling is a promising alternative to traditional refrigeration technologies based on compression cycles of greenhouse gases, which in addition to their obvious environmental threats cannot be scaled down to small sizes (e.g., microchip dimensions). However, most caloric materials known to date (ferroelastic, ferroelectric, and magnetic compounds) display only modest refrigeration performances and/or operate at temperatures that are distant from ambient conditions.

Recently, we have demonstrated with state-of-the-art simulation methods that giant caloric effects occur in fast-ion conductors [1-3], a class of materials with high ionic conductivity below their fusion points that commonly are exploited in electro-chemical devices. The giant caloric effects disclosed in fast-ion conductors can be understood in terms of field-driven changes on their ionic conductivity, which entail large entropy changes and are highly reversible and responsive to external fields. A giant cooling effect of about 20 K has been just measured directly in the archetypal superionic compound AgI [4]. We argue then that solid-state cooling could benefit immensely from the intensive research already undertaken in the field of solid-state batteries.


11:15 AM QN05.08.04
High Switching Ratio Thermal Switch Using a Peltier Couple Mark A. Verosky$^1$, Michael J. Adams$^1$, Joseph P. Heremans$^{2,3}$, and Mona Zeharjadi$^{4,5}$; $^1$Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, Ohio, United States; $^2$Department of Physics, The Ohio State University, Columbus, Ohio, United States; $^3$Department of Materials and Science Engineering, The Ohio State University, Columbus, Ohio, United States; $^4$Department of Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia, United States; $^5$Department of Materials and Science Engineering, University of Virginia, Charlottesville, Virginia, United States.

A critical design parameter of thermal switches is the ratio of between the thermal conductance in its on and off states; this parameter is denoted as the switching ratio. Most passive thermal switches rely on phase change material and operate only in small temperature regions. Active thermal switches usually require moving parts or vacuum seals. Here we propose an all-solid-state thermal switch with an adjustable switching ratio that can operate over a wide temperature range based on thermoelectric effects.

A switch was constructed from Bi$_2$Te$_3$-based materials and was characterized by its thermal conductance and response time. The switching ratio was calculated from the effective conductance measured in both open (no activation current) and closed switch (optimal activation current) configurations. This switching ratio correlates directly with the thermoelectric figure of merit ZT and diverges at small temperature difference. Switching ratios as large as 100 were found within the temperature range of $-20\,^\circ\text{C}$ to $140\,^\circ\text{C}$. The timed response can be predicted simply from the thermal resistance and capacitance.

11:30 AM QN05.08.05
Cross Interface Model for Thermal Transport through Cross Contact Xiaoxiang Yu$^1$, Yucheng Xiong$^2$, Dongyan Xu$^2$ and Nuo Yang$^1$; $^1$Huazhong University of Science and Technology, Wuhan, China; $^2$The Chinese University of Hong Kong, Shatin, Hong Kong.

The van der Waals (vdW) contact has emerged as a growingly important role due to their extensive presence in nanostructured materials and systems, such as assembled nanostructure building blocks array and vdW heterostructure, which recently shows massive potential as various functional electronic and optoelectronic devices. These applications require a thorough understanding of thermal transport through the vdW cross contact to address the increasingly severe heat dissipation problem in electronics. Here, we report on a systematic study of thermal transport through the vdW cross contact between individual copper phthalocyanine (CuPc) nanoribbons. We establish a brand new analytic model, cross interface model (CIM), for heat conduction across an interface with overlap, which is similar to the two-temperature model and the two-channel heat transport model, and apply the model to our experiments and numerical simulations. The experimental results by suspended thermal bridge methods reveal that the interfacial thermal conductance per unit area ($G_{th}$) between individual CuPc nanoribbons is on the order of $10^5\,\text{W/m}^2\cdot\text{K}$, which is two to five orders of magnitude smaller than that of the conventional solid-solid interfaces. Molecular dynamics simulations reproduce well the experimental results and suggest that the small $G_{th}$ was ascribed to the weak adhesion strength and the large separation distance of cross contact between CuPc nanoribbons. This work gives an analytic model for heat conduction in cross contact interface and points out that the deteriorative interfacial thermal transport between small molecular nanostructures remains significant bottlenecks for heat dissipation in related electronic devices.

11:45 AM QN05.08.06
Re-Thinking the Rules for Negative Thermal Expansion from First Principles—The Case Of PbTiO$_3$ Ethan T. Ritz and Nicole A. Benedek; Cornell University, Ithaca, New York, United States.

While most materials expand when heated, materials that exhibit negative thermal expansion (NTE) shrink when heated. NTE materials are critical in applications involving extreme thermal environments, such as inside gas turbine engines, computing hardware and spacecraft. However, while first observed experimentally over a century ago, the fundamental driving mechanisms behind NTE remain largely unknown for all but a handful of systems. One mechanism often invoked to explain NTE in inorganic framework materials and was characterized by its thermal conductance and response time. The switching ratio was calculated from the effective conductance measured in both open (no activation current) and closed switch (optimal activation current) configurations. This switching ratio correlates directly with the thermoelectric figure of merit $ZT$ and diverges at small temperature difference. Switching ratios as large as 100 were found within the temperature range of $-20\,^\circ\text{C}$ to $140\,^\circ\text{C}$. The timed response can be predicted simply from the thermal resistance and capacitance.

even though PbTiO$_3$ contains many RUM-like modes. Indeed, PbTiO$_3$ is unique among well-known NTE materials in that it appears to be the only materials that exhibits volumetric NTE well above room temperature and with positive Grüneisen parameters along all unique crystallographic axes. We find that the symmetry breaking distortion that drives the ferroelectric transition in PbTiO$_3$ also has a significant effect on both the elastic properties and lattice dynamics in general, and the NTE behavior of PbTiO$_3$ in particular. Our work has implications for the understanding of, discovery and design of NTE in perovskites and other families of inorganic materials.

### References

Several experiments have been carried out recently to better understand lattice and electronic thermal transport behaviors in three material systems. Based on steady-state differential measurements, the electronic thermal conductivity of h-BN/graphene/h-BN heterostructures deviate considerably from the Wiedemann-Franz law for both the bi-polar and single carrier type regimes and at both low and high temperatures, and the lattice thermal conductivity of graphene appears to increase when it is encased in h-BN compared to when it is supported on amorphous oxide. In addition, steady state electro-thermal and lock-in Raman thermometry measurements have found that the average thermal conductivity of millimeter size boron arsenide bulk crystals approaches the theoretical limit set by four-phonon scattering. Meanwhile, a multiple probe thermal transport measurements have observed a much weaker length dependence of the thermal conductivity of silicon germanium nanowires compared to a previous report, and the measurement results are in agreement with a first principles calculation.

4:00 PM QN05.10.01
Lattice and Electronic Thermal Transport in h-BN/graphene/h-BN Heterostructures, Boron Arsenide Bulk Crystals, and Silicon Germanium Nanowires Li Shi;
Department of Mechanical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, Texas, United States.

Several experiments have been carried out recently to better understand lattice and electronic thermal transport behaviors in three material systems. Based on steady-state differential measurements, the electronic thermal conductivity of h-BN/graphene/h-BN heterostructures deviate considerably from the Wiedemann-Franz law for both the bi-polar and single carrier type regimes and at both low and high temperatures, and the lattice thermal conductivity of graphene appears to increase when it is encased in h-BN compared to when it is supported on amorphous oxide. In addition, steady state electro-thermal and lock-in Raman thermometry measurements have found that the average thermal conductivity of millimeter size boron arsenide bulk crystals approaches the theoretical limit set by four-phonon scattering. Meanwhile, a multiple probe thermal transport measurements have observed a much weaker length dependence of the thermal conductivity of silicon germanium nanowires compared to a previous report, and the measurement results are in agreement with a first principles calculation.

4:30 PM QN05.10.02
Electrical and Thermal Transport Properties of Micron-Size Crystals Of Topological Kondo Insulator, Samarium Hexaboride (SmB6) Narayan Poudel1, Daniel Murray1, Jason Jeffries1 and Krzysztof Gofryk1; 1Idaho National Laboratory, Idaho Falls, Idaho, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States.

In the last 5 years the Kondo insulators have drawn a great interest in the field of strongly correlated systems. Special interest has been devoted to SmB6 that has been proposed to be a topological Kondo insulator at low temperature. Various electrical and thermal measurements have been performed on this material to explore its low-temperature insulating phase. These measurements often gave conflicting results due to the quality of the material used. To overcome these problems, we use micron-size single crystals prepared by plasma Focus Ion Beam (FIB) system and measure the thermal and electrical properties by specially designed experimental configuration. During the talk, I will present our experimental setup focusing on recent transport measurements of micron-size SmB6 crystals at low temperatures and high magnetic fields. I will discuss our results in the context of the presence of metallic surface states in this material. In addition, the thermal conductivity of the micron-size SmB6 crystals, measured by the 3w-method, will be presented and discussed.

4:45 PM QN05.10.03
Giant Enhancement in Rashba Spin-Seebeck Effect in NiFe/p-Si Thin Films Ravindra G. Bhardwaj2, Paul Lou1 and Sandeep Kumar1, 2; 1Mechanical Engineering, University of California, Riverside, Riverside, California, United States; 2Material Science and Engineering, University of California, Riverside, Riverside, California, United States.

The spin-Seebeck effect mediated thermoelectric energy conversion can provide an efficient alternative to traditional thermoelectrics for waste heat recovery. To achieve this goal, efficient spin to charge conversion using earth-abundant materials is essential. Proximity-induced Rashba effect arises from the charge potential mediated by structural inversion asymmetry, which has been reported in Si thin films and can be manipulated by controlling the thickness of the Rashba layer. We demonstrate a giant Rashba spin-Seebeck effect in NiFe/p-Si (polycrystalline) bilayer thin films. The bilayer thin film specimens have the p-Si layer thickness of 5, 25, and 100nm while keeping the NiFe layer thickness at 25 nm. The Rashba spin-Seebeck coefficient has been estimated to be 0.266 μV/K for 100nm p-Si, and increases by an order of magnitude to 2.11 μV/K for 5 nm p-Si. The measured spin-Seebeck coefficient in 5 nm p-Si specimen is one of the largest coefficients ever reported. The measured voltage of 100.3 μV is one of the largest reported spin-Seebeck voltages, with the smallest area of ~160×10 μm used in any spin-Seebeck measurement. This scientific and technological breakthrough using earth-abundant elements brings the spin mediated thermoelectric energy conversion for waste heat recovery closer to reality.
8:00 AM QN05.11.01
Nanoscale Simulation of Self Heating and Thermal Crosstalk in 3D finFET Architectures
Bjorn Vermeersch, Erik Bury, Kristof Croes, Herman Oprins, Hamed Kamrani and Geoffrey Pourniotis; imec, Leuven, Belgium.

Heat conduction in confined geometries and around small sources is known to no longer obey standard diffusion models. In contemporary electronic devices, where nanoscale active regions and extremely thin layers are widely prevalent, both effects combine and can induce junction temperatures that substantially exceed conventional predictions. Even so, virtually all commercial TCAD software carries out device-level thermal simulations using classical Fourier diffusion models with either nominal or phenomenologically adjusted thermal conductivities.

Advances in both theoretical understanding and computational power over the past decade have brought refined microscopic treatments within conceptual reach. Computational DFT and phonon Boltzmann codes such as VASP and ShengBTE have enabled researchers to model and predict direction and temperature dependent bulk thermal conductivity for a wide range of semiconductor compounds from first principles. The almaBTE platform subsequently extended these capabilities to analysing the thickness-dependent effective conductivity reduction in thin films and 1D Monte Carlo simulations of multilayer substrates.

In typical device geometries, however, thermal transport has a pronounced multi-dimensional character and occurs through a variety of material systems in which phonons are not always the dominant heat carriers.

Here, we report on the development of a custom thermal simulation platform that addresses the limitations of currently available tools. Our IMPALA framework brings quasielastic modelling capabilities to realistic TCAD settings. The solvers perform Monte Carlo simulation of 2D and 3D modular geometries using a hybrid materials modeling approach. The latter enables us to tackle, within one seamless particle-based simulation environment, the three types of compounds typically encountered in complex structures. Firstly, for semiconductors we employ wavevector-resolved phonon dispersions and scattering rates computed from first principles. These inherently capture the less efficient heat removal that arises in thin layers and around small active junctions. Secondly, metal contacts and electrodes are treated under the isotropic grey-medium BTE using estimated or measured values for the electron mean free path. Doing so naturally captures the size-dependent excess resistivity observed in narrow lines. Finally, heat flow in amorphous regions such as passivation/insulation layers is simulated by Brownian motion, thereby replicating diffusive transport at nominal bulk conductivity.

Practical applications for analysing front-end and back-end of line (FEOL/BEOL) self-heating and resulting thermal cross-talk in state-of-the-art finFET architectures will be discussed. 2D simulations already suggest the quasiballistic heat flow to have intricate repercussions on FEOL and BEOL reliability. The suppressed thermal performance of the transistor fins induces both a substantial increase in junction thermal resistance and stronger heat spreading along the drain electrodes. In turn, this raises the temperature in overhead metal lines, even near idle devices. Simulations of 3D structures, which are currently underway, can further elucidate the resulting impact on electromigration in the BEOL.

8:15 AM QN05.11.02
Understanding the Lattice Thermal Conductivity and Lorenz Number in Tungsten from First Principles
Yani Chen, Jinlong Ma and Wu Li; Shenzhen University, Shenzhen, China.

Tungsten is known to have a Lorentz number L larger than the Sommerfeld value Ls by 30%. By performing fully first-principles calculations, we are able to calculate the electronic conductivity (β) and quantify the electronic (κe) and lattice (κl) contributions to the thermal conductivity with a high accuracy. We show that the deviation of L is entirely due to κl. At room temperature κl is 46 W/m-K, one order of magnitude larger than that in other metals even with smaller atomic mass and higher Debye temperature, and likely the largest of all metals. The large κl is ascribed to the surprisingly weak anharmonic phonon scattering. The weak anharmonic phonon scattering is facilitated with the large atomic mass, leading to small thermal displacement.

8:30 AM QN05.11.03
Non-Cured Thermal Interface Materials with High Graphene Loading
Sahar Naghibi, Fariborz Kargar, Zahra Barani, Ruben Salgado, Dylan Wright and Alexander A. Balandin; Phonon Optimized Engineered Materials (POEM) Center, Department of Electrical and Computer Engineering, Materials Science and Engineering Program, Bourns College of Engineering, University of California., Riverside, California, United States.

Reliable affordable thermal management technologies remain a major packaging challenge driven by the continuous miniaturization of integrated circuits, increase of functionality of mobile devices, and growing computing density in data centers. Development of the next generations of thermal interface materials (TIMs) is important for packaging and thermal management of all electronic and optoelectronic devices. The discovery of the unique heat conduction properties of graphene [1] motivated numerous studies on the use of graphene and few-layer graphene in various composites. The most recent studies of thermal composites with graphene have been limited to curing epoxy-based composites [2-3]. However, TIM applications in thermal management of computers and other electronic gadgets, require non-cured TIMs. The Semiconductor Research Corporation (SRC) target for the thermal conductivity of TIMs is ~10 W/mK near room temperature. Despite substantial efforts and investments in research of new TIMs in the last couple of decades, there is no commercial thermal greases available with the verifiable thermal conductivity above 10 W/mK and the thermal interface resistances below 10 Kmm2/W. Commercial TIMs filled with conventional thermal conductive particles require large filler loading, >50% to achieve the thermal conductivity of the composite in the range of ~0.5 – 6 W/mK. In this presentation we report on development of the exfoliation and mixing techniques for preparation of the non-cured mineral-oil based composite with the commercially produced graphene flakes. The viscosity of the composites was kept in the range required for easy dispersion on the surfaces of interest. The lateral sizes of the few-atomic-layer fillers of graphene ranged from ~2 µm to ~15 µm while the thickness varied from single atomic planes of 0.35 nm to ~12 nm. The thermal conductivity of TIMs was determined using two types of industry standard TIM Testers (Longwin LW-9389 and Analysis Tech, Inc.), following the ASTM D5470-06 standard. It was found that the thermal conductivity of the graphene-based non-cured TIMs can exceed that of the best commercially available TIMs at substantially lower loading fraction. We will discuss the dependence of the thermal conductivity on the graphene loading characteristics, below and above the thermal percolation threshold. Brillouin – Mandelstam spectroscopy was used to determine the acoustic phonon velocities before and after graphene incorporation. Taking into account recent technological developments in the liquid phase exfoliation of graphene and various methods of reduction of graphene oxide, we argue that our results can open up new application domain for graphene in non-cured TIMs.

This work was supported, in part, by the National Science Foundation (NSF) through the Emerging Frontiers of Research Initiative (EFRI) 2-DARE award 1433395, and by the UC – National Laboratory Collaborative Research and Training Program LFR-17-47723.


8:45 AM QN05.11.04
Strong Phonon Anharmonicity of Type-I Clathrate Compounds
Masato Ohnishi1, Terumasa Tadano2, Shinji Tsuneyuki1 and Junichiro Shionoi1; 1The University of Tokyo, Tokyo, Japan; 2National Institute of Materials Science, Tsukuba, Japan.

Clathrate compounds are promising candidates for thermoelectric materials in terms of the “electron-crystal phonon-glass” concept. Because of strong anharmonic potential of guest atoms in cage structures of type-I clathrates, guest phonon modes lead to strong phonon scattering. Recently, first-principles simulations of phonon properties of a clathrate have been first demonstrated with using self-consistent phonon (SCP) theory that can include temperature-dependent fourth-order anharmonic interatomic force constants (IFCs) into harmonic IFCs [Tadano et al. Phys. Rev. Lett 120, 105901 (2018)]. Here, we reveal unusual anharmonic effects of phonons by comparing phonon properties of type-I Ba8Ga5O12X0.5 (X = Si, Ge, Sn, BGX) with first-principles simulations. We have first succeeded to calculate temperature-dependent thermal conductivities of BGXn with first-principles approach, which has the minimum thermal conductivity among the reported values of clathrates. Because the selection of atoms composing cage structures, namely Si, Ge, or Sn, manipulates the degree of anharmonicity, we have clearly observed effects of anharmonicity of phonons in clathrates. For example, we have observed an unusual effect of grain boundaries on phonon transport in BGXn; polycrystallization decreases a thermal conductivity of BGXn more at higher temperature.
Multi-Carrier Thermal Coupling at Heterogeneous Interfaces

Energy and mass transport across grain boundary determines the physical property of materials. The emerging grain boundary engineering methods coupled with laser-based acoustic spectroscopy and thermal transport could offer a new route to study the microstructure of polycrystalline ceramics for novel applications. Here, we employ the time-domain Brillouin spectroscopy (TDBS) to non-invasively monitor acoustic phonon propagation inside individual grains and detect the microstructure of polycrystalline cera, an important electrolyte material in solid oxide fuel cells. TDBS employs a conventional pump-probe technique based on femtosecond laser. The pump beam launches bulk acoustic waves propagating away from the surface and a time-delayed probe beam detects propagation of these acoustic waves. Strong longitudinal waves are readily observed whose velocity agrees with theoretical calculations. Large amplitude shear waves are generated through mode conversion when a thin layer of gold is deposited with matched acoustic impedance. Amplitude of measured shear phonon exhibits strong dependence on optical polarization of the probe beam. A theoretical model that accounts for the generation, propagation, and detection of acoustic phonons is developed to explain these observations. Additionally, the capability of TDBS to image grain microstructure non-destructively through deep substrate measurement of Brillouin oscillation frequency is demonstrated. The grain orientations at the surface are obtained and compared with the results from electron backscatter diffraction technique (EBSD). The subsurface morphology of grain boundary is constructed in 3D nondestructively, unlike traditionally used EBSD that requires destructive sequential analysis. The current work paves the path for future study on phonon/grain boundary interaction and offers guidance for material design in advanced energy systems.

Giant Effect of Spin-Lattice Coupling on the Thermal Transport in Two-Dimensional Ferromagnetic CrI

Recently, two-dimensional monolayer chromium triiodide (CrI) with intrinsic magnetism was experimentally discovered, which shows promising applications in many technologies ranging from sensing to data storage where thermal transport plays a critical role. However, so far, the effect of spin-lattice coupling on the thermal transport properties has not been explored yet. In this talk, we present the giant effect of spin-lattice coupling on the lattice thermal conductivity ($\kappa$) of monolayer CrI. The lattice thermal conductivity is more than two orders of magnitude enhanced by considering the spin-lattice coupling. The effect is found to be especially stronger for the acoustic phonon modes, which dominates thermal transport with spin-lattice coupling. The mechanism lies in the weakened phonon anharmonicity by spin-lattice coupling. The bond angle and atomic position are changed due to the spin-lattice coupling, making the structure much stiffer and more symmetric, which lead to the weaker phonon anharmonicity, and thus the enhanced thermal conductivity. This study uncovers the effect of spin-lattice coupling on the thermal transport, which would deepen our understanding on thermal transport and shed light on future research of thermal transport in magnetic materials.

Multi-Carrier Thermal Coupling at Heterogeneous Interfaces

Efficient heat transfer is one of the major concerns in the design of micro- and nano-scale materials and devices. In metals, electrons and phonons both carry significant thermal energy, whereas in semiconductors and dielectrics phonons are the dominant carriers. Therefore, for metal-semiconductor composite structures, heat can transfer across an interface by coupling either between phonons in metal and dielectric or by direct coupling between electrons in metal and phonons in dielectric through electron-interface scattering. Phonon-phonon coupling at interfaces has been well studied, mainly by the acoustic mismatch model (AMM) and the diffuse mismatch model (DMM). For electron-phonon coupling at and near hetero-interfaces, a number of different viewpoints exist. Some studies have assumed that electron-phonon coupling across a metal-dielectric interface is negligible, and heat transfer occurs as electron-phonon coupling within metal and then phonon-phonon coupling across the interface. Electron-phonon coupling at metal-dielectric interfaces has been measured to exhibit negligible apparent thermal resistance in some cases, yet other times it has been suggested to be important [e.g., for Pd-diamond]. In recent work we have shown that, with accurate definition and understanding of atomic structure, the electron-phonon coupling across silicide-silicon interfaces must include rigorous first-principles understanding of electron-phonon coupling (e.g., via the Eliashberg function) both within the metal and in the near-interface region of the semiconductor in order to obtain close quantitative agreement with experiments [1], [2]. In summarizing the current state of this topic, it would be reasonable to conclude that some qualitative understanding is emerging on cross-interface electron-phonon coupling, but that quantitative models validated by experiments remain scarce. Here, we discuss a new innovation – namely interfaces with tunable interfacial heat transfer characteristics to assess the relative contributions of different carriers and coupling mechanisms. As another example, electron-phonon coupling in bilayer graphene controls its unique photoconduction response. We find that, in contrast to single-layer graphene, $\Gamma$ point LA’ and TA’ modes in bilayer graphene couple strongly with electrons with energies lower than 200 meV, while optical modes dominate in the high electronic energy range. A Drude model of photoconductivity provides good agreement with experiments for both the real and imaginary components. Finally, we discuss a rigorous temperature-dependent approach involving Green-Kubo equilibrium spiral and atomic dynamical properties to assess phonon-magnon interactions in magnetic solids. Resulting predictions of the non-electronic thermal conductivity of iron show very good agreement with experimental measurements. By computing the modal phonon-magnon scattering rates, the high-frequency phonon-magnon scattering rates are found to be one order magnitude larger than those at low frequencies regions due to energy conserving rules and the high density of states. This new framework fills existing gaps in simulating thermal transport across the ferro/para-magnetic transition.

References
the wave vector. A force constant is a derivative of the total potential energy of the system with respect to the displacement of a given atom. Accurate methods to compute these quantities are needed without the approximations inherent in finite difference methods.

In this paper, we present the automatic code differentiation technique to perform unintrusive sensitivity analysis and derivative computation in nanoscale phonon transport simulations. This method exploits the concepts of templating and operator overloading in C++ and other similar programming languages to unintrusively convert existing codes into those yielding derivatives of arbitrary order. The idea is demonstrated through the computation of phonon properties such as second and third order force constants, the Gruneisen parameter, group velocities, and the temperature sensitivity of specific heat for graphene nanoribbons. Derivative values so computed are compared with those obtained using finite difference approaches or with analytical values. The method is found to yield derivative values to machine accuracy, with none of the round-off issues associated with finite difference approaches.

11:00 AM QN05.12.02
Deducing Phonon Modes from Atomistic Simulations
Antan Raj and Jacob Eapen; Nuclear Engineering, North Carolina State University, Raleigh, North Carolina, United States.

Normal modes are non-interacting, non-decaying collective excitations of atomic vibrations. Many-body atomistic dynamics with an arbitrarily accurate anharmonic Hamiltonian provides a direct approach for probing the interactions among the crystal normal modes. The traditional normal mode analysis (NMA) framework, which employs complex normal mode coordinates, does not, however, distinguish the non-resistive normal (N) phonon interactions from the resistive Umklapp (U) interactions. By adopting a set of real asymmetric normal mode coordinates, we show that both N and U processes can be resolved directly from atomistic simulations.

Although the normal modes exchange energy continuously, they are localized in the reciprocal space and engage in discrete interactions. Interestingly, we observe that the harmonic and anharmonic energies do not remain constant. The time-dependent Hamiltonians, which is an intrinsic property of all anharmonic lattices even at low temperatures, can allow a multitude of normal mode interactions that are not possible with constant anharmonic energies. Using graphene as a model material, we show the emergence of normal modes that are created and annihilated simultaneously. We anticipate that such additional scattering channels can be discovered with more complex Hamiltonians using the current approach. Finally, we discuss the correspondence between the normal modes extracted from atomistic simulations and the quantum phonon modes that are employed in Boltzmann transport equation (BTE).

11:15 AM QN05.12.03
Unconventional Impact of Thermal Phonon Coupling in Film-On-Substrate Systems
Kartik S. Kothari, Abhinav Malhotra and Martin Maldovan; Georgia Institute of Technology, Atlanta, Georgia, United States.

An accurate determination of thermal transport in thin film-on-substrate (FOS) architectures is crucial to optimum performance of nanostructured devices. A rigorous treatment of the nanoscale interfacial thermal coupling between materials accounting for dispersion mismatch, interfacial roughness and shadowing effects is imperative in studying the impact of substrates on thin-film conduction. We demonstrate novel thermal functionality in FOS systems, creating a new paradigm for thermal management in optoelectronic applications. In a breakthrough finding, we discover an increase in thermal conductivity with a reduction in thin-film thickness attributed to phonon injection from the substrate layer. We examine the in-plane and cross-plane configurations of thermal conduction in Ge and Al_{0.5}Ga_{0.5}As thin-films mounted over Si and GaAs substrates respectively. We provide an extensive analysis of phononic coupling and contrast the results with bulk and isolated thin film values. We present a detailed microscopic and spectral analysis by investigating the spatial thermal flux distribution, modal thermal conductivity, and mean free path and frequency spectra in the FOS architecture. We elucidate how interlayer phonon coupling opens new avenues for thermal conductivity manipulation in nanostructures and achieves desired thermal properties for rational thermal material design in microelectronics and optoelectronics.

11:30 AM QN05.12.04
3D Silicon Meta-Lattices with Low Thermal Conductivity and Bulk Electrical Transport

Nanostructured thermoelectrics are currently emerging as promising materials for energy generation due to their improved thermoelectric efficiency via increasing contribution of complex nano-interfaces to the decreasing thermal transport through them. However, lack of 3D order and connectivity restricts the flow of electrons and phonons through the structure. But, theoretical predictions of electrical and thermal properties through periodically arranged nanoporous silicon suggests significant improvement in performance of such thermoelectric devices. In the present work, a 3D ordered and precisely doped Si nanostructure, namely an inverse opal metalattice, with periodicities on the order of 1-100 nm is synthesized using unique infiltration of Si into the voids of closely packed silica spheres nanotemplates through high pressure confined chemical vapor deposition. Subsequently, Time domain thermoreflectance method is utilized to measure the thermal transport through these structures as a function of sphere size ranging from 14-100nm and observe the effect of interfacial thermal resistance and appropriately control it to strive towards higher thermoelectric figure of merit. Initial data on intrinsic Si inverse opals show a significant reduction in thermal conductivity with values lying close to or lower than fused silica indicating a dominant interface effect on phonon transport through these structures. Secondly, occurrence of a minima at 20nm sphere size further points towards the role that geometry has on phonon scattering mechanism while travelling through them. Theoretical understanding of the phonon transport mechanism and subsequent studies of thermal transport with respect to variation of geometry, composition and porosity will be performed to aim towards potential thermoelectric applications of these structures.

References

11:45 AM QN05.12.05
Engineered Particle-Particle Contacts for High Thermal Conductivity Soft Polymer Composites
Matthew Ralphs, Wilson Kong, Robert Wang and Konrad Rykaczewski; Arizona State University, Tempe, Arizona, United States.

Thermal interface materials (TIMs) are arguably the solution to faster and smaller computer chips. As integrated circuits get faster and smaller, it becomes more difficult and paramount to remove the excess heat. TIMs accomplish this by dramatically reducing the contact resistance between IC components so heat can be better conducted away from the chip. The most common way to make a TIM is to add high conductivity particles to a polymer matrix, which boosts the thermal properties of the base polymer material. However, the interfacial thermal boundary resistances between the particles and matrix ($R_{pp}$) and the particles themselves (particle-particle resistance, $R_{pp}$) prevent the high k particles from passing heat through the matrix effectively. In this presentation, we will discuss a two-step process for resolving this issue: inducing particle percolation using magnetic alignment and engineering of their contacts using shell structures that minimize $R_{pp}$. Maximum particle-particle contact is achieved by magnetically aligning the fill material in the polymer matrix. The applied magnetic field seggregates particles into aligned columns within the polymer matrix, enforcing percolation and ensuring good contact between particles. We show that magnetic alignment of the particles alone doubles the thermal conductivity of the composite ($k$) over the unaligned composites, even without any special consideration for the particle-particle interfaces. With the particles in good contact with one another, particle contact engineering can then have the greatest effect in boosting $k$. We use silver and liquid metal particle coatings to decrease $R_{pp}$ of solid nickel particle fill by providing a layer that can plastically deform and increase the particle-particle contact
area. Dry powder beds show a decrease of more than 4× in thermal resistance with a silver shell thickness of only a few hundred nanometer and 500 kPa force to “sinter” the powders together. Similarly, liquid metal is used as a coating for the nickel particles and shows a similar decrease in thermal resistance but requiring a larger amount of liquid metal for an equivalent reduction in thermal resistance.

Applying these engineered contacts in a magnetically aligned polymer composite maximizes the benefits of the silver and liquid metal coatings by enforcing good particle-particle contacts throughout the polymer matrix. We demonstrate that the magnetically aligned silver coated nickel particles produce almost an extra 2× increase in k over the aligned nickel particles at volumetric fill ratios of 0.4 and 0.5 with an 8vol% silver shell. The aligned liquid metal coated nickel show small increases in k over the aligned nickel particles until the volume of liquid metal to Ni reaches 50%, where a 2.5× increase is achieved over the aligned nickel composite at a particle volume fill fraction of only 0.3. The mechanisms are discussed and a full parameter space is explored to fully evaluate these engineered contacts and minimize Rp/n.

Work has been conducted on the laser patterning of graphene and 2D thin transition metal dichalcogenide (TMDC) films. Laser thinning has been performed in conjunction on-line diagnostics to precisely control the film thickness. Tuning the properties of atomic layer films by modulating the free carrier type and density and composition can offer an exciting new pathway to various practical nanoscale electronics. Our laser induced doping process is spatially local and selective, and the doping level is widely tunable by varying the duty cycle and laser irradiation. Moreover, laser doping can be digitally controlled and is an air-stable process for achieving fabrication of high-quality, high-fidelity nanodevices. Sharp and high quality P-N junctions have been demonstrated, and using laser thinning of liquid metal nanodevices has been developed, aiming at decoupling the vacancy formation, precursor gas decomposition and dopant incorporation processes. Controlled doping of graphene and TMDC films has been demonstrated via this approach. Time-resolved probing with femtosecond resolution has been conducted to understand the transport properties of the ultrathin films and the effects of doping and defect formation.

The transient thermal grating (TTG) technique, in which two crossed laser pulses produce a spatially periodic temperature profile whose decay is monitored with a probe laser beam, is widely used for thermal transport measurements. On the one hand, this technique provides a non-contact method of measuring thermal diffusivity with intrinsically high absolute accuracy. On the other hand, it offers a tool for studying heat transport at small distances without the need to fabricate nanostructures, with the heat transfer distance controlled by the TTG period. However, the latter cannot be made smaller than half the optical wavelength, thus limiting the ability to study thermal transport on the nanometer scale. This difficulty can be circumvented by using an extreme ultra-violet (EUV) laser source. TTG measurements in the EUV range (13-50 nm) are now possible at the FERMI free electron laser facility (Elettra, Trieste, Italy). In this report, we will describe the first measurements of thermal transport with thermal gratings produced by EUV light performed at FERMI. In the initial series of measurements, we used EUV excitation (12.7 nm) and optical probe (400 nm) to study thermal transport in single crystal silicon and diamond sample at a TTG period of 280 nm, corresponding to a heat transfer distance of ~90 nm. We find that in silicon the heat transport is strongly non-diffusive but still does not reach the ballistic limit. In diamond the heat transport is found to be close to the purely ballistic regime. The results will be compared with calculations based on the Peierls-Boltzmann phonon transport equation using scattering rates calculated from first principles. We will also describe the first measurements with EUV light used for both excitation and probing, which made it possible to shrink the TTG period to 25 nm (heat transfer distance ~8 nm). The EUV probe has an additional advantage of being insensitive to electronic excitations, which simplifies the interpretation of the measurements. Further prospects for using EUV transient gratings to study thermal transport on the single-digit nanometer scale will be discussed.

Thermal energy dissipation and transport processes influence the physical properties of matter, control the kinetics of chemical reactions, and trigger bio-molecular mechanisms in living organism. Understanding how thermal phenomena arise and change as the characteristic length scale of structures becomes comparable to or even shorter than the mean free path of energy carriers such as electrons and phonons is therefore on of the key challenges in the physical sciences. In this talk, we will first provide an overview of the numerous scanning probe based thermal nano-imaging and spectroscopy methods developed to quantify local energy dissipation and thermal transport phenomena in nanoscale systems and molecular structures. We will highlight the unique capabilities of thermal scanning probe techniques to unravel local dissipation processes down to few-nanometer length scales, and discuss prospects to extend existing thermal imaging approaches towards characterization of collective dissipation processes in quantum material systems. Secondly, we will present recent experiments extending traditional scanning thermal microscopy towards nanoscale spectroscopy. We will illustrate how local photo-thermal forces in tip-sample nanocavities enable to study energy dissipation in molecular systems with simultaneous chemical specificity. We will illustrate how to separate thermally induced expansion from optical forces and provide guidelines for the development of new thermal nanoimaging modalities combining local scanning probe with tunable laser excitation.

Individual luminous nanoparticles enable temperature measurements with sub-diffraction limited spatial resolution. While single-particle measurements require excitation intensities orders of magnitude higher than nanoparticle ensembles, potential single-particle self-heating effects remain largely uninvestigated because thermal models predict negligible self-heating. We show that the common “ratiometric” thermometry single of individual 50 x 50 x 50 nm3NaYF4:Yb3+:Er3+ nanoparticles increases unexpectedly with excitation intensity, implying a temperature rise over 50 K if interpreted as thermal [1]. Luminescence lifetime thermometry results indicate a similar temperature rise. We resolve this apparent contradiction between model and experiment by systematically varying the nanoparticle’s thermal environment: the substrate thermal conductivity, nanoparticle-substrate contact resistance, and nanoparticle size. The apparent self-heating remains the same in all cases, demonstrating that this effect is an artifact rather than a true temperature rise. Using established rate equation models, we show that this artifact is instead due to increased radiative and non-radiative relaxation from higher energy Er3+ manifolds.

Following calibration of this apparent self-heating effect, individual NaYF4:Yb3+:Er3+ nanoparticles can be employed as accurate nanothermometers. We demonstrate the ability of 50 x 50 x 50 nm3 NaYF4:Yb3+:Er3+ nanoparticles to characterize nanoscale hotspots and sharp temperature gradients using two different modalities. First, by coating a low thermal
conductivity substrate with an optically absorbing metal film, we can achieve substantial local heating and measure the peak temperature within a laser-heated spot using a single exciting laser beam. Our nanoparticle thermometer minimizes spatial averaging of the temperature profile, thereby increasing the accuracy of this temperature measurement relative to thermometry techniques with coarser resolution. We also measure the spatial temperature variation within the laser-heated spot. Additionally, we Joule heat microfabricated metal structures to create sharp temperature gradients via “current crowding” effects caused by geometric constrictions. We then quantify the temperature variation in these structures. Our measurements demonstrate that individual NaYF₄:Yb³⁺:Er³⁺ nanoparticles can be used as nanoscale thermometers in scenarios ranging from fundamental thermal measurements to device-level applications.


2:45 PM QN05.13.05

Nanothermometry and Nanocharacterization in Scanning Thermal Microscopy—Approach Curves and Temperature Jumps at Contact Ali Alkuri1, Axel Pic2, Aloise Guen3, Antonin M. Massoud1, Wenyu Zhao1, Jan Martinek1, Christophe Lucchini1, Rodolphe Vaillon1, Sebastien Gallois-Garreignot2, Matthieu Bugnet1, Petr Klapetek1, Jean-Marie Bluet1, Séverine Gomès1 and Pierre-Olivier Chapuis3; 1CNRS - INSA Lyon, Lyon (Villeneuve), France; 2ST Microelectronics, Crolles, France; 3CMi, Brno, Czechia; 4IES, Madrid, Spain.

Scanning thermal microscopy (SThM) is a key thermal characterization tool, where a micro to nanometer-scale probe tip measures the temperature close to a surface. The spatial and temperature resolutions of this technique are limited in particular by the size of the tip, the sample properties, and the various tip-sample heat transfer mechanisms [1] depending on the operation conditions. In this communication, we present a study of heat transfer between a sample surface and a SThM probe based on resistive thermometry: the probe electrical resistance depends on the probe temperature. Such probe operates either in thermometry (passive) mode with a minimal Joule self-heating to enable sample surface temperature measurement or in thermal-property measurement (active) active mode where a significant Joule heating is needed to allow thermal power flowing into the sample, depending on its thermal conductivity.

We first study the hot tip-cold sample (active mode) heat exchange as a function of the tip-sample distance [2]. When the tip is far from the surface (>100 micrometers), it is cooled by heat convection and there is no exchange with the sample. At lower distances, the diffusive heat exchange starts. The exact geometry is required to compute accurately the transfer, which can be done by means of Finite Element Modeling (FEM). In the sub-micrometer distance regime, air conduction cannot be modeled by usual FEM because the air mean free path (~60 nm) is on the order of the average distance between the hot object and the sample. In our simulations, we account for this deviation to the diffusive regime by adding thermal resistances on surfaces, which correspond to the ballistic transfer limit in air. This allows us to reproduce numerically the ballistic leveling off seen experimentally. Depending on the probe considered, a 1D approximation [3] or improved considerations based on the Boltzmann transport equation for air molecules are to be taken into account.

When the tip and the sample are in contact, heat transfer is enhanced, which is described by the contact thermal conductance. It includes contributions from the solid-solid mechanical contact, the water meniscus around the mechanical contact and the constrictions in the heat flux path. In the best cases, this thermal contact is responsible for 5% of the total tip temperature decrease due to the tip-sample exchange. We discuss the impact of various tips with curvature radii ranging from a micron down to 10 nm, especially the ballistic thermal dissipation in the sample, and the impact of vacuum-condition operation, where air transfer is removed. In addition, the modest impact of the applied force on the heat exchange is observed.

In a second step, we consider SThM thermometry (passive mode). There are two key phenomena to account for. First, the probe temperature is not equal to that of the sample, as the cantilever base acts as a heat sink which imposes a temperature distribution in the tip. Second, since the tip acts partially as a heat sink which is placed close to the sample, it modifies the sample temperature distribution. Accounting for this effect can be crucial, as highlighted by experiments performed with samples heated by means of Joule-heated electrically-resistant serpentines.

We believe that this work, where both the understanding of the physical mechanisms responsible for thermal transport between the tip and the samples and precise knowledge of the energy balance of the tip-sample systems are targeted, provides a decisive step for determining quantitative data from the experiments.

References:

Acknowledgements:
The support of projects TIPTOP (ANR-16-CE09-0023), DEMO-NFR-TPV (ANR-16-CE05-0013), QUANTIHEAT (FP7-2012 604668), EFINED (H2020-FETOPEN-1-2016-2017 766853), THERMOS (INSA-BQR-2017) is acknowledged.

3:00 PM BREAK

SESSION QN05.14: Thermal Materials for Batteries, Buildings and Wearable Applications
Session Chairs: Yongjie Hu, Yee Kan Koh, Lucas Lindsay and Amy Marconnet
Thursday Afternoon, April 25, 2019
PCC North, 100 Level, Room 124 B

3:30 PM QN05.14.01

Decoupling Phononic and Electron Temperatures in Thermionic Power Converters Nicki Hogan, Shengxiang Wu and Matthew Sheldon; Texas A&M University, College Station, Texas, United States.

Our laboratory is interested in taking advantage of plasmonic properties for thermionic power converters. The benefit to using these metasurfaces comes from the additional population of photo-excited non-thermal ‘hot’ electrons on top of traditional photothermalization. Thermionic emission current increases as a function of temperature, however practically devices are limited by the melting point of the metal. This significantly hinders possible power conversion applications. By decoupling the electronic and phononic temperature in nanostructured films we can increase the electronic temperature to a regime where there is efficient emission without destroying the device.

We show how anti-Stokes Raman spectroscopy can independently measure the phononic and electronic temperature. This allows for us to demonstrate the changes in the electronic temperature in response to excitation wavelength but also changes in nanostructure geometry. Phononic temperatures from the nanostructures under laser excitation vary from 300-500 K, well below the melting point of the structures, while electronic temperatures range above 5000 K. These electronic temperatures are high enough to promote efficient electron emission in a temperature range where the device is still thermally stable.

We verify that device power conversion matches our temperature measurement by constructing a simple thermionic device by pairing the metasurface with an ITO anode and measuring current across the vacuum gap between the two. We demonstrate that a gold film, which has fewer hot electrons at electronic temperatures <2000 K, shows no measurable current. However, nanostructured surfaces lead to a short circuit current of 0.015 A*cm² under continuous wave illumination of 10⁶ W/m². Correlating the temperature and the measurement gives information about the lifetime of a hot electron as well as the electron-phonon coupling that we correlate to other ultra-fast time resolved studies.
Thermoelectric Generators (TEGs) can continuously convert human body heat into electricity. Therefore, they can eliminate the usage of chargeable batteries in wearable devices. The next generation of self-powered devices come up with controlling the performance of thermoelectric materials and device together. For body wearable TEGs the performance is limited by the hot side (skin) and cold side (ambient) heat exchangers as they experience high parasitic resistances to the body [1]. This requires the TEG to be designed with not only careful consideration of material properties, but also specific consideration of module design, particularly the fill factor and contact resistance. Most of current research is focused on improving the thermoelectric material properties to enhance the efficiency of the TEGs while poor design of the TEG module can produce parasitic resistances that can reduce the generating power on body condition.

To improve the performance of the TEG device, the thermal resistance of the module should be much higher than parasitic resistances. The module thermal resistance can be increased by reducing the thermal conductivity of the legs, increasing the aspect ratio of the legs, and reducing the filling factor (number of the legs in unit area) of the module. Designing low fill factor TEGs will reduce the production cost, while it improves the generated output power in comparison to a high fill factor TEGs. The maximum output power for a wearable TEG made of high thermal conductivity materials (~1.5 W/mK) achieves at lower fill factors (<10%), however, making low fill factor modules is quite challenging. In this research, we designed a TEG with very small fill factor (3%) and compared it with other modules with different fill factors. The power generation characteristics of the modules were studied in practical environment. The results confirm the concept of generating high power with low fill factor module [1]. Therefore, the output power per unit mass can be maximized in comparison to the commercial off-the-shelf TEG.

Reference:
Porous Polymer Coatings with Fluid-Mediated Optical Switching—A Diverse Platform for Optical and Thermal Regulation

Nanorarchitectured metamaterials that enable spatial control of heat flow have innumerable benefits in as daytime radiative cooling, thermal textile, and thermophotovoltaic systems. Their abilities to tune in plane heat transport and out of plane thermal emission has been of tremendous interest in adaptive tuning of optical channels in response to environmental changes.

In this invited talk, I will present our ongoing efforts on nanorarchitectured thermal metamaterials that are enabled by scalable 3D nanofabrication technology. For example, we recently demonstrated an on-site nano-kirigami method by programming the dosages of the ion beam irradiation in one step. A remarkable 3D optical chirality is achieved through the out-of-plane twisting by nano-kirigami, leading to selective angular emission of circularly polarized IR photons several orders of magnitudes higher than that in natural chiral materials. I will also discuss the potential of thermal metamaterials for detection of chemically induced phase transitions and 3D nanophotonic control of thermal radiation.

Ulta-Narrowband Wavelength-Selective Thermal Emitter and Absorber with Multi-Layered Metamaterials Designed by Bayesian Optimization

We computationally designed ultra-narrowband wavelength-selective thermal emitter and absorber via a materials-informatics method alternating between Bayesian optimization and thermal electromagnetic field calculation. For a given target infrared wavelength, the optimal structure was efficiently identified from over 8 billion candidates of multilayers consisting of multiple components (Si, Ge, and SiO$_2$). The resulting optimized structure is an aperiodic multi-layered metamaterial exhibiting high and sharp emissivity with the Q-factor of 273. The designed metamaterials were then fabricated, and reasonable experimental realization of the optimal performance was achieved with the Q-factor of 188, which is significantly higher than those of structures empirically designed and fabricated in the past. This is the first demonstration where metamaterials designed by Bayesian optimization is realized in experiments. The results facilitate the machine-learning-based design of metamaterials and advance our understanding in the narrow-band thermal emission mechanism of aperiodic multi-layered metamaterials.

Porous Polymer Coatings with Fluid-Mediated Optical Switching—A Diverse Platform for Optical and Thermal Regulation

Porous polymers, which vary in their intrinsic electromagnetic behavior and morphology, are a diverse platform for optical and thermal management. For instance, porous poly(vinylidene fluoride-co-hexafluoropropene) (P(Vdf-HFP)) coatings exhibit near-perfect solar reflectance $R_{solar}$ ($>$ 0.96) and long-wave infrared (LWIR) emittance $\varepsilon_{LWIR}$ ($>$ 0.97) for radiative cooling [1], while porous poly(ethylene) (PE) films exhibit high $R_{solar}$ ($>$ 0.8) and LWIR emittance $\varepsilon_{LWIR}$ ($>$ 0.6) useful in thermal management designs with tuneable $\varepsilon_{LWIR}$ [2]. However, making such coatings optically dynamic remains to be explored in detail.

In this presentation, we demonstrate that the optical behaviors of porous polymers can be dramatically altered by reversibly wetting and drying them with index-matched fluids. For porous P(Vdf-HFP), the drastic reduction of the scattering efficiency of the pores upon wetting causes transition from a solar reflective to a transparent state. The coatings, which show remarkable $\Delta R_{solar}$ of 0.74, can be deployed in roofs, walls and windows for large scale adaptive radiative cooling, solar heating and daylighting depending on the time of day or season. Extending the concept to ethyl cellulose, we show that hydrophilic porous polymers can act as water-responsive coatings that can be used for warming houses before rain or in situations requiring applications and underground watercooling. Lastly, we show that porous PE-based designs wetted with IR emissive fluids can achieve large and opposite $\Delta R_{solar}$ of 0.3 and $\Delta \varepsilon_{LWIR} = -0.6$, representing an "ice-house" to "green-house" transition useful for tunable radiative cooling at night and potentially, thermal camouflaging. Promisingly, the optical performances are achieved over a fast switching time ~ 1 min, and are stable over large number of cycles. The performances of the porous polymer coatings are either new, or better than or comparable to notable electrochromic and thermochromic designs [2-4]. However, unlike the latter, they combine a passive functionality with active switching. Importantly, the porous polymers and fluids used are readily available and inexpensive. Given these aspects, porous polymers with fluid-activated optical switching are a promising and sustainable paradigm for optical and thermal regulation.
A fundamental series of thermal conductivity measurements using time domain thermoreflectance (TDTR) have been performed on photonic (phonon-glass) HKUST-1 Metal-Organic Frameworks (HKUST-1 SURMOFs) thin films. We have determined the thermal conductivity of loaded and unloaded (pristine) HKUST-1 thin films in dependence of their film thickness. These monolithic, polycrystalline HKUST-1 SURMOF thin films are grown using liquid phase epitaxy (LPE) grown at different film thicknesses on specially modified Au and Al SiO2 substrates. In addition, infiltrated MOFs have been measured to determine the effect of loading with different organic solvents, water, and TCNQ. The experimental results demonstrate a reduction in the thermal conductivity upon the polar guest molecule infiltration compared to the pristine activated MOFs. The bulk modulus of the thin, pristine HKUST-1 SURMOF was also measured to understand how the negative thermal expansion of this material affects the temperature dependent mechanical and thermal properties. These materials have been presented here as tunable Designer Materials for the generation of novel porous phononic Nanomaterials with unexpected and tailorable physical properties for high-efficient thermoelectric generation and future applications.

9:45 AM QN05.15.06

Colloidal nanocrystal solids are widely used in a variety of applications due to their unique electronic, optical and magnetic properties. However, nanocrystal solids have very low thermal conductivities (0.1-0.5 W m$^{-1}$K$^{-1}$), which presents a challenge for heat dissipation in nanocrystal solid-based electronic and photonic devices. The low thermal conductivity of nanocrystal solids originates from numerous interfaces in their internal structure. The ligand-ligand interfaces between adjacent nanocrystals are especially problematic because of the weak van der Waals (vdW) interactions at these locations.

We show that forming covalent bonds at these ligand-ligand interfaces can significantly increase thermal conductivity in colloidal nanocrystal solids. More specifically, we demonstrate a thermal conductivity increase of 200-300% in iron oxide nanocrystal solids via crosslinking of adjacent oleic acid ligand molecules. Crosslinking of the oleic acid molecules on nanocrystal surface is carried out through a moderate thermal anneal (350 °C) and is confirmed through a combination of x-ray photoelectron spectroscopy, mass spectrometry, and nanoindentation experiments. The nanoindentation experiments demonstrate that this cross-linking process increases the Young’s modulus of the nanocrystal solid from 1.4 GPa to 9.5 GPa. This correlates to a sound velocity increase from 1243 m s$^{-1}$ to 4290 m s$^{-1}$ that in turn helps increase thermal conductivity.

We use the differential 3 omega method to measure the cross-plane thermal conductivity of our nanocrystal solid samples as a function of nanocrystal diameter. These measurements indicate that ligand-cross-linking increases the thermal conductivity of these samples by a factor of 2-3. This is in approximate agreement with effective medium approximation (EMA) modeling that predicts a factor of 3. We also use molecular dynamic simulations to confirm that ligand cross-linking alleviates a key thermal transport bottleneck in these materials. These results collectively suggest that the key to improve the thermal transport in nanocrystal solids lies in improving thermal transport across the ligand-ligand interface.

Reference:

10:00 AM BREAK

SESSION QN05.16: Thermal Management for Multi-Devices
Session Chairs: Yongjie Hu, Yee Kan Koh, Lucas Lindsay and Amy Marconnet
Friday Morning, April 26, 2019
PCC North, 100 Level, Room 124 B

10:30 AM QN05.16.01
Modeling and Measurement of Electrothermal Effects in Wide Bandgap Semiconductor Devices Samuel Graham; Georgia Institute of Technology, Atlanta, Georgia, United States.

Wide bandgap electronics made from nitrides (e.g., Gallium Nitride (GaN)) and oxides (e.g., Hafnium Oxide (HfO2) and Gallium Oxide (Ga2O3)) are currently under development due to their potential to create some of the most advanced RF, power electronic, and neuromorphic computing devices in the world. However, the thermal response of these devices under applied electric fields can create large power densities (RF and power electronics) or highly non-linear behavior (neuromorphic devices) that must be understood.

For many of these devices, the electrothermal response plays a strong role in both the acceptable operation or long-term failure and reliability of the devices. Thus, tools that can help elucidate these responses and provide a method to help design better devices is of critical need for this field.

In this talk we will discuss advancements in modeling and thermal characterization techniques that have allowed new insights into electrothermal behavior in HfO2, GaN and Ga2O3 materials and devices. Specifically, a focus on the role of device architecture and material processing will be addressed. For GaN and Ga2O3 RF and power electronics, the role of thermal interfaces in the heat dissipation of both lateral and vertical device architectures will be discussed. Unique thermoreflectance imaging of cross sectioned devices will show for the first time the experimental picture of the electrothermal response of devices such as pn diodes as current and heat flow through the electrical contacts. For neuromorphic devices, the use of electrically driven filament formation will be elucidated through multiphysics modeling and high spatial resolution thermal imaging. These models will be used to determine methods in which low power formation and operation of neuromorphic devices can be obtained.

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11:00 AM QN05.16.02
Thermal Boundary Conductance Across Heteroepitaxial GaN Interfaces—Scattering Mechanisms and Assessment of the Phonon Gas Model Patrick Hopkins1, John Gaskins2, George Kotsonis3, Ashutosh Giri1, Samuel Graham1, Tengfei Luo4, Asegun Henry5, Mark S. Goorsky5, Junichiro Shiom3 and Jon-Paul Maria5; 1University of Virginia, Charlottesville, Virginia, United States; 2The Pennsylvania State University, State College, Pennsylvania, United States; 3Georgia Institute of Technology, Atlanta, Georgia, United States; 4University of Notre Dame, Notre Dame, Indiana, United States; 5Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 6University of California, Los Angeles, Los Angeles, California, United States; 7The University of Tokyo, Tokyo, Japan.

We present experimental measurements of the thermal boundary conductance (TBC) from 78 – 500 K across isolated heteroepitaxially grown ZnO films on GaN substrates. This data provides an assessment of the underlying assumptions driving phonon gas based models, such as the diffuse mismatch model (DMM), and atomistic Green’s function (AGF)
formalisms used to predict TBC. Our measurements, when compared to previous experimental data, suggest that TBC can be influenced by long wavelength, zone center modes in a material on one side of the interface as opposed to the “vibrational mismatch” concept assumed in the DMM; this disagreement is pronounced at high temperatures. At room temperature, we measure the ZnO/GaN TBC as 490[+150, −110] MW m−2 K−1. The disagreement among the DMM and AGF, and the experimental data at elevated temperatures, suggests a non-negligible contribution from other types of modes that are not accounted for in the fundamental assumptions of these harmonic based formalisms, which may rely on anharmonicity. Given the high quality of these ZnO/GaN interfaces, these results provide an invaluable, critical, and quantitative assessment of the accuracy of assumptions in the current state of the art computational approaches used to predict phonon TBC across interfaces. We then extend our understanding to measurements across other interfaces of GaN.

11:15 AM QN05.16.03
Nonstructured Interfaces by Random Nanopillars Enhance Interfacial Thermal Transport Eunghyu Lee, Erezdhep Menumerov, Robert Hughes, Svetlana Nerusina and Tangfei Lu; University of Notre Dame, Notre Dame, Indiana, United States.

Solid-state interfaces are pivotal to the high performance in semiconducting electronic devices ranging from GaN-based high-electron mobility transistors to light-emitting diodes. While unprecedented electrical loads are on such electronic devices to maximize their capability, the interfaces usually impede efficient heat removal with large thermal boundary conductance (TBC). For example, in power electronics, generated heat fluxes from semiconducting channels have reached (or exceeded) 1 GW/m². It leads to temperature rises in the channels up to 100 °C, where half of the temperature rise can be from various interfaces. Recently, it has been reported that nonstructured interfaces with periodic nanopillar arrays significantly increase thermal transport across semiconductor/metal interfaces. In this study, we demonstrate that random-distributed nanopillars interfaces fabricated by low-cost Au islands metallic etching masks can enhance TBC of semiconductor/metal interfaces, where the Au islands mask is prepared by thermal solid-state dewetting (TSSD) properties of Au on solid substrates. We first confirm that Si/Al nonstructured interfaces with randomly and periodically distributed Si nanopillars have similar enhanced thermal transport across the interfaces when their interfacial area enhancement -- which are accurately controlled by electron-beam lithography -- are almost same. Such finding suggests distribution of nanopillars at interfaces are not critical to thermal transport enhancement, motivating us to find low cost methods to fabricate randomly distributed nanopillars on solid substrates. As a result, we apply the TSSD method to prepare random nanostructured Si surfaces where the Si nanopillars have characteristic lengths ranging from 10 nm to 70 nm. By capping these nanostructured Si surfaces with Al layer, it is found that the TBC of these randomly nanostructured Si/Al interfaces is ~ 90% higher than that of planar interfaces. In addition, the nonstructured Si/Al interfaces maintain the enhancement at a temperature range from 30 °C to 110 °C, in which semiconducting electronics usually work. Moreover, we successfully extend the TSSD technique to GaN surfaces and demonstrate thermal transport enhancement across GaN/Al interfaces similar to the cases for Si/Al interfaces. The TSSD technique can potentially reduce the cost to achieve random nanostructured interfaces over large areas. Commercial applications can take advantage of our results in enhanced interfacial thermal transport to improve thermal management.

11:30 AM QN05.16.04
Thermal Management in Silicon Integration Fabric (Si-IF) Umaesh Mogera and Timothy Fisher; Henry Samueli School of Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Moore’s law of packaging calls for several innovations in advanced packaging. One approach is the direct placement of silicon dies, heterogeneously, on a single interconnected platform, termed ‘Silicon Interconnect Fabric’ (Si-IF) [1-2]. In this approach, interconnect pitch can be reduced by almost 100 times (~10 µm) [3], which is impossible to achieve by conventional packaging technologies. However, such high placement density of dies requires enormous power density (~1-10 W mm²) which in turn generates huge heat load on the system. Therefore, such a dense but large system will need efficient thermal dissipation to avoid thermal degradation of performance and to ensure reliability. This calls for an efficient power interconnect architecture to the Si-IF that delivers not only power but also manages thermal loads generated in Si-IF. Here, we propose an approach, called PowerTherm that combines these two functions uniquely and efficiently. The PowerTherm concept involves a network of current-delivering blocks with built-in cooling that is dynamic and addressable. The architecture of PowerTherm consists of metallic terminal blocks such as Cu bonded to Si-IF by thermo-compression bonding and optimized copper-filled electrically insulated through-wafer-vias (TWVs) that pass through the entire thickness of the Si-IF (500 µm) to contact the terminal block. For thermal management, macroscopic channels are constructed into the metallic terminal blocks through which cooled liquid is passed. We use a dynamic and ultra-high-flux capable flash cooling method with two-phase coolants that produces peak heat transfer coefficients of 50,000 W/m²K [4]. For testing of thermal management of Si-IF by flash cooling, we developed a dynamically controlled flow loop. The loop has been designed to be flexible and robust at various test conditions to quantify and benchmark the flash cooling of Si-IF. A detailed characterization of heat dissipation density and transient thermal response of the Si-IF were carried out in this study.

References:

11:45 AM QN05.16.05
Thermal Conductance Across Heterogeneous GaO3-Diamond Interfaces Zhe Cheng1, Marko J. Tadijer2, Virginia D. Wheeler3, Jingjing Shi1, Luke Yates1, Mark S. Goorsky1, Karl D. Hobart2, 3 and Samuel Graham1; 1Georgia Institute of Technology, Atlanta, Georgia, United States; 2U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 3Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Because of its ultra-wide bandgap, high electrical breakdown strength, and potential for large area substrates, b-GaO3 has attracted great attention recently for applications of high power electronics. However, its thermal conductivity is at least an order of magnitude lower than that of other wide bandgap semiconductors, such as SiC, GaN, AlN, and diamond. Proper thermal management is essential to avoid device degradation for high-voltage applications. A possible solution is to integrate thin GaO3 layer to fabricate GaO3-on-diamond devices by taking advantage of the ultra-high thermal conductivity of diamond as a heat spreader and wide bandgap dielectric substrate. When dissipating heat generated in a device through a diamond substrate, the thermal boundary resistance (TBR) of the GaO3-diamond interface can play an important role in the thermal response. The contribution of the TBR in this heterostructure has not been studied yet. In this work, we study thermal transport across several GaO3-diamond interfaces, including exfoliated GaO3-single crystal (SC) diamond van der Waals interface, chemical-vapor-deposited diamond grown on a sc (~201)GaO3-commercial substrate (Tamara Corp.), as well as atomic-layer-deposited GaO3 on SC diamond. The thermal boundary conductance (TBC) of these interfaces were measured by time-domain thermoreflectance (TDT) and the structures of these interfaces are studied with transmission electron microscopy (TEM). For instance, the TBC of exfoliated GaO3-SC diamond van der Waals interface is measured to be 17 MW/m²K. To understand the measured TBC values of different GaO3-diamond interfaces, a Landauer approach is used to calculate the theoretical TBC of GaO3-diamond interfaces. An electron energy loss spectroscopy (EELS) study is performed across the GaO3-diamond interfaces with nanometer spatial resolution to probe the vibrational mode. Our work is the first study to perform thermal conductance across different GaO3-diamond interfaces. These experimental and theoretical studies would not only contribute to developing new theories of interfacial thermal transport, but also impact applications such as high power electronics.

SESSION QN05.17: Thermal Transport in Nanomaterials
Session Chairs: Yongjie Hu, Yee Kan Koh, Lucas Lindsay and Amy Marconnet
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 124 B

A novel fabrication method for an imperceptible transparent electrode based on copper random micro patterns is introduced in this work. This fabrication method enables minimum spot size of 2.4-μm and elimination of Motre and starburst effect by employing the randomness of the pattern, in turn an imperceptible transparent electrode especially for display devices or thermoelectric devices can be made. The cost of fabrication of the transparent electrode introduced in this study is much lower than other well-known fabrication methods which use noble materials such as silver nanowires since the process is all solution based process and only Cu nanoparticles are used as a conducting medium. Thermal conducting layer is introduced to successfully sinter Cu nanoparticles. The performance of imperceptible transparent electrode based on copper random nanopatterns made by fabrication method introduced in this work, a resistive type touch panel application and defroster application is also demonstrated.

1:45 PM QN05.17.02
Energy Sensitivity Studies of Charge-Carrier Scattering in Graphene Antidot Lattices Dongchao Xu1, Samuel Tang2, Xu Du1 and Qing Hao1; 1University of Arizona, Tucson, Arizona, United States; 2SUNY Poly, New York, New York, United States; 3Department of Physics & Astronomy, Stony Brook University, Stony Brook, New York, United States.

Understanding the scattering mechanisms of charge carrier is critical to the electrical properties of two-dimensional materials such as graphene, transition metal dichalcogenide monolayers, black phosphorene, and tellurene. Beyond pristine two-dimensional materials, further tailored properties can be achieved by nanoporous patterns such as nanor- or atomic-scale pores (antidots) across the material. As one example, structure-dependent electrical/optical properties for graphene antidot lattices (GALs) have been studied in recent years. However, detailed charge carrier scattering mechanism is still not fully understood, which hinders the future improvement and potential applications of such metamaterials. In this work, the energy sensitivity of charge-carrier scattering and thus the dominant scattering mechanisms are revealed for GALs by analyzing the maximum Seebeck coefficient with a tuned gate voltage and thus shifted Fermi level. It is found that charge carriers are mainly scattered by the potential field due to edge-trapped charged, particularly at elevated temperatures. For thermoelectric interests, the gate-voltage-dependent power factor of different GAL samples are measured and can reach 554 at 400 K for a GAL with the square pattern. For on-chip cooling applications, such a high power factor is improved by more than one order of magnitude from the values for the state-of-the-art bulk thermoelectric materials. With their high thermal conductivities and power factors, these GALs can be well suitable for “active coolers” within electronic devices, where heat generated at the hot spot can be removed with both passive heat conduction and active Peltier cooling.


2:00 PM QN05.17.03
Substrate Effects on Thermal Transport in Single-Layer MoS2 Alexander J. Gaborie1, Saurabh V. Suryavanshi1, Amir Barati Farimani1 and Eric Pop1,2; 1Electrical Engineering, Stanford University, Stanford, California, United States; 2Materials Science & Engineering, Stanford University, Stanford, California, United States; 3Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Two-dimensional (2D) semiconducting MoS2 is a promising material for end-of-roadmap technologies [1], flexible and transparent electronics [2], and thermoelectric applications [3]. However, it is known that electrical and thermal conductivities in other 2D materials, like graphene, degrade when in contact with a substrate, e.g. due to scattering with substrate impurities or phonons [4, 5]. Such insulating substrates cannot be avoided in modern electronics; therefore, understanding the role of the substrate is crucial to know the realistic thermal limitations of 2D semiconductors like MoS2.

Here, we present a detailed molecular dynamics (MD) study on the effects of an amorphous SiO2 (a-SiO2) substrate on the in-plane thermal conductivity of single-layer MoS2. Unlike continuum models, the atomistic nature of MD accurately captures phonon scattering physics in 2D materials and their interfaces. The GPUMD package [6, 7] is used for all MD computations and thermal conductivity calculations use the recently-developed homogenous non-equilibrium MD (HNEMD) method [8]. HNEMD results are consistent with the equilibrium Green-Kubo and non-equilibrium MD methods but require fewer computational resources. The in-plane thermal conductivity is decomposed into its in-plane and out-of-plane contributions to elucidate which phonons are suppressed. We also present a spectral decomposition of the thermal conductivity for insight into the phonon wavelengths affected by the substrate.

To facilitate comparison, we compute the in-plane thermal conductivity of both isolated, single-layer MoS2 and single-layer MoS2 on an a-SiO2 substrate. The simulation cell area is 10 × 10 nm², the single-layer MoS2 is 6.15 Å thick, and the a-SiO2 substrate is 5.4 nm thick. The in-plane dimensions are periodic, with vacuum in the out-of-plane direction. All simulations are at 300 K with a time step of 0.5 fs.

Running 20 independent simulations for each structure, we first calculate the suspended single-layer MoS2 in-plane thermal conductivity to be ~115 Wm⁻¹K⁻¹ (consistent with experimental measurements on bulk MoS2) [9] with the in- and out-of-plane contributions as ~84 Wm⁻¹K⁻¹ and ~31 Wm⁻¹K⁻¹ respectively. The in-plane thermal conductivity of MoS2 supported by an a-SiO2 substrate is calculated to be ~29 Wm⁻¹K⁻¹ (~74% decrease) with the in- and out-of-plane contributions as ~25 Wm⁻¹K⁻¹ (~70% decrease) and ~4.7 Wm⁻¹K⁻¹ (~85% decrease) respectively. While a greater proportion of the out-of-plane component is suppressed on a-SiO2, the in-plane component’s reduction drives the overall reduction in thermal conductivity. This contrasts the suppression of the in-plane thermal conductivity of graphene on a-SiO2, which suffers ~91% degradation mostly from the suppression of the out-of-plane component [10]. Our results underscore the strong effect of the substrate on thermal conductivity of single-layer 2D semiconductors like MoS2 for the first time.

6. Z. Fan et al., Computer Physics Communications 218, 10-16 (2017).
7. Z. Fan et al., Computer Physics Communications 184, 1414-1425 (2013).
8. Z. Fan et al., arXiv:1805.00277 [cond-mat.mtrl-sci].

2:15 PM QN05.17.04
Heat at the Nanoscale—A Comprehensive Experiment Testing Specific Thermal Behavior from Nanoparticles Mengistie L. Debasu1,1, Artemi Skripka2, Carlos Brites1, Antonio Benayas1,1, Fiorenzo Vetrone3 and Luis Carlos4; 1Physics, CICECO, Aveiro, Portugal; 2EMT, INRS, Varennes, Quebec, Canada; 3Radiology -MIPS, Stanford School of Medicine, Stanford, California, United States.

Nowadays, there is an ever-growing wave of reports providing cumulative evidence about a behavior of heat transport in solids at nanoscale that may substantially divert from the well-known physical laws governing thermal conductivity at macroscopic (bulk) size range.1 Thus, the opportunity is wide open to unveil a much more comprehensive insight on how the adage “more is different” can work also in the opposite direction. If so, a scientific turning point lies ahead, once ascertained if certain laws of nature may work through a different path when considered at ultrashort range domain.

In the other hand, luminescent nanothermometry has become a powerful investigative tool able to report temperature real-time, from inside complex systems in a smart non-contact way. Based on a thorough understanding of how emission lines from the luminescent nanoparticles change depending on temperature variations, these so-called nanothermometers report local temperature readouts grasped from the spectroscopic measurement of the light emitted from them, upon optical excitation. This research field has produced substantial progress and applications, especially at the biomedical sensing arena.

In this work, we present a simple nanothermometry set up -already used for successful studies on brownian movement- to measure the average time profile of temperature changes inside a given kind of luminescent nanoparticles. Appropriately, the nanoparticles have been engineered to constitute high-resolution nanothermometers, able to distinguish in real-time the differentiated temperature from two physically separated points, at the inside of the nanoparticles. Thus, that described framework allows us to record the (averaged) time evolution of the temperature inside the nanoparticles.

A quartz cuvette containing core-shell nanoparticles suspended in water was heated from one side in thermal contact with a thermofoil heater. The temperature of the suspension was increased by adjusting the temperature of the heater and the evolution of corresponding upconversion emission spectra of the suspended nanoparticles was recorded upon excitation with a 980nm-laser. The core and shell temperature profiles were determined, respectively, by using the integrated intensity ratios of the Er\(^{3+}\):\(H_{5/2}\rightarrow3I_{7/2}\) and \(G_{5/2}\rightarrow3H_{5/2}\) transitions as thermometric parameters, with temperature resolution \(<0.5K\) and relative thermal sensitivity up to \(1.25%K^{-1}\). Hence, this experimental procedure allows to measure precisely two distinct onset times with delay time up to 250 sec the core and shell temperature increments when a core-shell nanoparticle is heated by an external heating source and to thoroughly study the corresponding thermal transport dynamics in nanosystems. The experimental process is also gifted with high repeatability of the measure values. The data mining, once carefully treated with error correction numerical protocols, translates into a great wealth of heat transport insight (20-50 nm distance through crystalline lattice).

The conclusions produced from the collected data will undoubtedly help clarifying trends on the different behavior of the thermal diffusivity at nanoscale in solids, compared to the one foreseeably expected from the (macroscopic) heat diffusion laws in solids. This presented method paves the way for adapting new theoretical formulations of heat transport, also featuring different implications spread into physics, microelectronics and biology.

REFERENCES


2:30 PM QN05.17.05 Tuning the Phonon Transport in PbTiO\(_3\) Thin Films Through Strain-Engineered Domain Wall Configurations Eric Langenberg1, Dipanjana Saha, David Bugallo Ferrón, Jian-Jun Wang2, Elias Ferreiro-Viča1, Megan Holtz3, Hanjong Paik1, David A. Muller1, Long-Qing Chen, Gustau Cufalda, Nena Döring1, Jonathan A. Maken1, Darrell Schlom1, Francisco Rivadulla1; 1Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2CQUS, Universidade de Santiago de Compostela, Santiago de Compostela, Spain; 3Mechanical Engineering Department, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 4Department of Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; 5School of Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; 6Catalan Institute of Nanoscience and Nanotechnology, Bellaterra, Barcelona, Spain; 7Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York, United States.

Materials with tunable phonon transport are a key ingredient to achieve logic operations using heat currents. Moreover, the corresponding variation of the thermal conductivity can be used to greatly enhance the thermoelectric properties and, therefore, promoting the development of new thermoelectric materials. In this regard, ferroelectrics are excellent candidates to be explored as they possess intrinsic interfaces –domain walls– which effectively act as phonon scattering centers and their distribution and type can be engineered, for instance, by epitaxial strain. In pursuit of this goal, we report the effect of the strain-engineered domain and superdomain structures in ferroelectric PbTiO\(_3\) on the thermal conductivity.

PbTiO\(_3\) thin films were grown by reactive molecular-beam epitaxy on SrTiO\(_3\), DyScO\(_3\), TbScO\(_3\), and SmScO\(_3\) substrates, covering epitaxial strain values from compressive -1.36% to tensile +0.71%. For large compressive strains PbTiO\(_3\) thin films with only c-domains are obtained. At these compressive strain values, the absence of the presence of an electrostatic boundary condition (an epitaxially grown bottom electrode) switches from a \(c\)/up domain architecture to a \(c\)/down configuration with 180° domain walls to a single \(c\)-domain sample that contains no domain walls. On reducing the compressive strain, a gradual increase in the population of \(a\)/domains embedded in a matrix of \(c\)-domains takes place, giving rise to \(a\)/c domain architectures. The density of these \(a\)/c 90° domain walls increases on reducing compressive strain. For tensile strains a competing scenario between \(a\)/c and \(a\)/a superdomains is found in which the ratio between both populations can be tuned by varying strain. This enabled the superdomain architecture to be engineered at will. The density of 90° domain walls between the \(a\) domains within the \(a\)/a2 superdomains was found to increase with increasing tensile strain.

The thermal conductivity of PbTiO\(_3\) thin films is strongly influenced by these designed ferroelectric nanostructures. When no domain walls are present, relatively high thermal conductivity is obtained: \(>3.4\) Wm\(^{-1}\)K\(^{-1}\), similar to bulk values. The thermal conductivity, however, dramatically drops (<70% reduction) when a high \(a\)/a2 domain wall density in an \(a\)/a2 superdomain configuration is achieved. A clear correlation between thermal conductivity and domain wall density/type is found, giving rise to a huge control of further tuning the thermal conductivity of PbTiO\(_3\) through epitaxial-strain-engineered domain configurations. These results agree with the theoretical prediction from phase-field modeling, which were performed without previewing the experimental data. The combination of theory and experiment allows gaining a deeper understanding of this phenomenon that relates strain-designed domain structures and thermal conductivity.

2:45 PM QN05.17.06 Enhancing the Thermal Transport Properties of Soft Materials Using Nanoparticles Merabia Samy1,2, Chenxi Ma1, Haouie Han1, Frédéric Leroy3 and Florian Müller-Plathe1; 1Université de Lyon, CNRS, UCLL, ILM, UMR5306, Villeurbanne, France; 2CNRS, Villeurbanne, France; 3Technische Universität Darmstadt, Darmstadt, Germany.

In this contribution, we shall illustrate through two examples how the addition of a tiny amount of nanoparticles may significantly change the thermal transport properties of soft materials. Of particular importance here are the coupling between phonons in the solid and high frequency vibrations in the liquid [1].

First, we analyze heat transport between gold and a model ethanol nanofluid using molecular dynamics simulations [2]. We show that the presence of the nanoparticles increases the Kapitza resistance typically by a factor 2. Surprisingly, the interfacial resistance is found to depend only weakly on the interactions between the nanoparticles and the gold surface. This increase has important consequences as regards ultrafast explosive boiling, and we report on a significant shift of the nanofluid/gold boiling temperature as compared to pure ethanol. The corresponding superheating shift is found to be strongly correlated with the increase of Kapitza resistance.

Second, we demonstrate how the presence of a few nanoparticles may enhance the thermal conductivity of amphorous polymers [3]. Indeed, polymer are renowned for their low cost, low weight and resistance to corrosion. Yet, a barrier which limits the spread and use of polymers in a wide range of applications, and especially in microelectronics, is their relative poor thermal conduction properties. Dispersing highly conductive nanoobjects in a polymer matrix is a common strategy employed to level off polymer conductivity. However, the results are often mitigated by the high Kapitza resistance between the polymer matrix and the dispersed fillers. Here, we report a significant increase of the bulk conductiviy of polystyrene matrix filled with silica nanoparticles. We show that the relative enhancement is essentially explained by the relative good matching between the vibrational modes of the polymer and the silica nanoparticles. We discuss also the role of polymer chains grafted on the surface of the nanoparticale.

References:

**Unified First Principles Theory for the Thermal Properties of Semiconductors**

The availability of fabricating new mesoporous materials opens the possibility of having materials with tunable properties such as thermal conductivity. In this work, we present two applications of a generalized effective medium approximation that allows modeling of the thermal properties of porous systems.

A simple composite system is made of a homogenous matrix with a fixed number of parallel cylindrical holes of circular cross-section. By defining the two-dimensional depolarization factor for the cross-section of the cylinders, we calculate the effective thermal conductivity. For a system with a fixed number of pores, we show how the heat transport depends on the eccentricity of the pores. This is a full calculation that includes the heat resistance at the pore-matrix interface (Kapitza resistance). The method is applied to deformable porous media. By applying a mechanical stress to the system, the distance between the nanopores changes as well as their shape, initially with a circular cross-section. We find an expression for the effective heat coefficient as a function of the applied mechanical stress.

For a set of layered systems, each layer made of a mesoporous system. In particular, we consider as a second example the calculation of the heat transport coefficient of a stack of a mesoporous TO2 layer and mesoporous SiO2 layer, validating our model with recent measurements. (1)


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**Phonon Scattering by an Atomic Vacancy in IV-VI Semiconductors from an Ab Initio Green's Function Method**

Encompassing diffusive, quasi-ballistic and ballistic regimes, heat conduction is inherently a multiscale problem. At the atomistic level, the phonon mean-free-path (MFP) distribution is typically obtained by density functional theory. On the other side, phonon-boundary interaction is conveniently captured by continuum models, such as the Boltzmann transport equation (BTE). Finally, short-MFP phonons will mostly travel diffusively, so they can be accounted for by a standard diffusive solver. OpenBTE [1] attempts bridging these three regimes. Specifically, the MFP distribution, computed by first-principles, is used as input to the MFP-BTE [2], a recently introduced version of the BTE that uses the phonon MFP as a control variable. Then, using a parameter-free multiscale approach, the BTE solver integrates a modified diffusive model that calculates heat carried by short-MFP phonons. After a brief introduction to the software architecture, we will show example applications, including thin films, nanoporous materials, Graphene nanoribbons, Si serpentes, phonon focusing and large-scale screening of nanostructured materials for thermoelectric applications. Conclusions and final remarks will conclude the talk.

1. [www.openbte.org](http://www.openbte.org)

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**Phonon Scattering from an Atomic Vacancy in IV-VI Semiconductors from an Ab Initio Green’s Function Method**

Defects engineering has been a widely used approach for developing low thermal conductivity materials. Also, for some materials (e.g., IV-VI compound), considerably large amount of vacancies was often observed in single crystalline samples. The atomic vacancy in dilute case was assumed as a point defect that can cause the Rayleigh scattering with its rate proportional to the fourth power of phonon frequency. Due to the large dependence of scattering rate on phonon frequency, a vacancy was considered to only weakly suppress the mode thermal conductivity of low frequency acoustic phonons. We show that this does not hold for IV-VI materials. We compare the phonon scattering by a single vacancy in group IV (diamond and Si) and IV-VI (PtTe and GeTe) crystals using an exact ab initio Green’s function approach. The phonon-vacancy scattering rates in diamond and Si follow the well-known fourth-power dependence on phonon frequency. However, PtTe and GeTe exhibit phonon scattering rates that have much weaker frequency dependence. As a result, a vacancy scatters low frequency acoustic phonons more strongly in PtTe and GeTe than in Si and diamond. This unusual behavior in PtTe and GeTe originates to the significant changes of interatomic force constants that extend up to the distance of 10 angstrom from the vacancy site. Therefore, a vacancy in IV-VI materials cannot be assumed as a point defect but its finite size should be considered for phonon scattering. In contrast, a vacancy in Si and diamond changes interatomic force constants only up to 3 angstrom range. Our study provides new insights on the phonon spectral contribution to thermal transport when vacancies exist in IV-VI materials and will help to develop low thermal conductivity materials by engineering vacancies.

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**Unified First Principles Theory for the Thermal Properties of Semiconductors**

In semiconductors, heat is carried by phonons, which are quantized vibrations of the crystal lattice. Standard first principles methods to obtain the thermal properties of solids rely on the phonon quasiparticles being well-defined, and assume that the lowest order interactions among three phonons are sufficient to describe thermal transport. Here we show that this is not the case for strongly anharmonic semiconductors, where phonon scattering is so strong that the standard phonon quasiparticle picture can break down, and three-phonon scattering is insufficient to explain the experiments. To address this issue, we present a novel first principles method that features an anharmonic many-body renormalization scheme to create well-defined phonon quasiparticles with weakened interactions, and rigorously accounts for both three-phonon and four-phonon scattering to obtain thermal transport properties [1]. Using a showcase strongly anharmonic material – sodium chloride (NaCl), we demonstrate that our first-principles method simultaneously captures the apparently contradictory experimental measurements of low thermal conductivity and large lattice thermal expansion of NaCl on the one hand, and the relatively temperature-independent phonon frequencies on the other, while the standard first principles theory fails in all three cases. Furthermore, we show that the higher-order four-phonon scattering significantly lowers the thermal conductivity of NaCl and should be rigorously included for a proper comparison to measurements. Finally, we show that our anharmonic renormalization theory, along with four-phonon scattering, also successfully captures the phonon spectral contribution to thermal transport due to the material’s temperature-dependent thermal transport properties of a weakly anharmonic material – diamond, although the four-phonon scattering and renormalization effects are weak in this material. Our work presents a unified first principles framework to accurately predict the thermal properties of solids with varying bond anharmonicities.


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**Origin of High Thermal Conductivity in Complex Molecular Crystals—An Ab Initio Study of Polythiophene**

This work was partially supported by Solid State Solar-Thermal Energy Conversion Center (S3TEC), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0010929/DE-FG02-09ER46577 (phonons and thermal expansion) and by the Office of Naval Research MURI, Grant No. N00014-16-1-2436 (thermal conductivity).

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**Origin of High Thermal Conductivity in Complex Molecular Crystals—An Ab Initio Study of Polythiophene**

Peishi Cheng, Austin J. Minnich and Nina
Thermally conductive molecular crystals are of fundamental and practical interest in part because they are unlike typical complex crystals, which conduct heat poorly owing to their large phonon scattering phase space. While molecular crystals with high thermal conductivity in the range of tens of Wm\(^{-1}\)K\(^{-1}\) have been known experimentally for decades, the microscopic origin of this property has remained unclear. Ab-initio methods that have been successfully applied to simple crystals have proved difficult to adapt to molecular crystals due to quantum nuclear motion and their complex primitive cells. Here, we report the thermal transport properties of crystalline polythiophene with 28 atoms per primitive cell using an ab-initio approach that rigorously includes finite temperature anharmonicity and quantum nuclear effects. The calculated room temperature thermal conductivity is 176 Wm\(^{-1}\)K\(^{-1}\), a high value that arises from exceptional phonon focusing along the chain for certain branches and despite short lifetimes in the picosecond range. Our finding suggests that many complex molecular crystals with stiff intra-chain bonds are intrinsically good thermal conductors as phonon focusing occurs in any crystal with anisotropic bonds.

**SYMPOSIUM QN06**

Emerging Materials for Quantum Information  
April 23 - April 25, 2019

Symposium Organizers  
Jelena Klinovaja, University of Basel  
Peter Krogstrup, University of Copenhagen  
Christopher Richardson, University of Maryland  
Javad Shabani, New York University

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* Invited Paper

**SESSION QN06.01: Topological I**  
Session Chairs: Peter Krogstrup and Javad Shabani  
Tuesday Morning, April 23, 2019  
PCC North, 100 Level, Room 127 B

10:30 AM *QN06.01.01*  
**Majorana in Atomic Chains and Topological Hinge States**  
Ali Yazdani; Princeton University, Princeton, New Jersey, United States.

Ettore Majorana famously considered that there may be fermions in nature that are their own antiparticle — and then he mysteriously disappeared just after proposing the idea in 1938. In recent years, following pioneering theoretical work of Kitaev and others, we have learned how to engineer materials that harbor quasiparticles that behave similar to fermions Majorana had envisioned. In particular, there has been a focus on one-dimensional topological superconductor that harbor Majorana zero modes (MZM) that can potentially be used to make fault-tolerant topological quantum computation possible. Recently, we have proposed and implemented a platform for realization of topological superconductivity and MZM in chains of magnetic atoms on the surface of a superconductor [1,2]. In this talk, I will describe this platform and the series of experiments we have performed to establish the presence of these exotic quasi-particle using spectroscopic mapping with the scanning tunneling microscope (STM). [2-4] These include study of the unique spin signature of MZM.[4] Finally, if there is time I will discuss our most recent work on realization of MZM in a platform based on chiral quantum spin Hall edge states [5]. Overall these experiments, illustrate how the power of spectroscopic imaging with the STM can be used to visualize novel quantum states of matter and their exotic quasi-particles.

References  

11:00 AM *QN06.01.02*  
**Majorana and Andreev Bound States in Proximitized Rashba Quantum Wires**  
Daniel Loss; Department of Physics, University of Basel, Basel, Switzerland.

I will review recent theoretical developments in the field of topological quantum computing, in particular, I will focus on schemes based on Majorana fermions. For Majorana physics, a central ingredient is the proximity effect induced by a superconductor in some attached material. In particular, semiconducting quantum wires defined within 2DEGs and strongly coupled to thin superconducting epitaxial layers have been extensively explored in many experiments as promising platforms to host Majorana bound states. I will present our numerical and analytical studies of such geometries with proximity effects [1-5] where the strong coupling can lead to unwanted ‘metallization’ of the semiconductor host. I will also show that Andreev bound states in absence of any topological phase can mimick the zero-energy behavior of Majorana bound states as function of magnetic field [6].

References  

11:30 AM *QN06.01.03*  
**Emergence of Majorana States in Engineered Atomic-Scale Hybrid Systems**  
Roland Wiesendanger; Interdisciplinary Nanoscience Center Hamburg, University of Hamburg, Hamburg, Germany.

Majorana states in atomic-scale magnet-superconductor hybrid systems have recently become of great interest because they can encode topological qubits and ultimately provide a new direction in topological quantum computation [1,2]. First, it will be demonstrated how well defined 1D atomic chains of magnetic adatoms on superconducting substrates with high spin-orbit coupling can be artificially fabricated using STM-based atom-manipulation techniques. Spin-polarized STM measurements [3] allow to reveal the presence of non-collinear spin textures, i.e. spin spiral ground states, stabilized by interfacial Dzyaloshinskii-Moriya interactions [4,5]. Simultaneously performed scanning tunneling spectroscopy on the magnetic atom chains on the superconductor substrate reveal the evolution of the spatially and energetically resolved local density of states as well as the emergence of zero-energy bound states at the chain ends above a
critical chain length. Based on the exact knowledge of the geometrical, electronic, and spin structure of the magnetic chain – superconductor hybrid system, the experimental results can be compared rigorously with ab-initio and model-type tight-binding calculations supporting the interpretation of the spectroscopic signatures at the ends of the chains as Majorana bound states [6]. More recently, the atomic-scale design of more complex network structures for Majorana state manipulation, including braiding operations has been in the focus of our research.

Second, we will address experimental and theoretical studies of monolayer topological superconductivity and chiral Majorana edge modes in model-type 2D magnetic islands on elemental superconductors [7]. In particular, we demonstrate that interface engineering by an atomically thin oxide layer is crucial for driving the studied hybrid system into a topologically non-trivial state as confirmed by theoretical calculations of the topological invariant, the Chern number.

Finally, the prospects for studies of Majorana states in skyrmion – superconductor hybrid systems [8] will be highlighted.

We will first report on the growth developments of InSb two-dimensional electron gas (2DEGs) on GaAs (100) substrates. These structures exhibit high carrier mobility up to

directly apply the signatures of MZMs (basically conductance peaks) into real devices for quantum computing, as up to date, the total number and stability of the created qubits

to modify its properties at will, e.g.: hybrid semiconductor-superconductor nanowire based quantum networks.

the material’s topological phase is a fundamental requirement to achieve the Majorana Zero Modes (MZMs), and for them to materialize it is mandatory to create thoroughly

InSb nanowires are used to detect first signatures of quasi particles called Majorana fermions. Recently, different schemes for performing operations and uncovering the non-

scattering that can prevent the transition or even the failure of the topological regime. Incredible efforts are being made to avoid the so unwanted decoherence of the electrons and

Relevant material platforms for MZM based devices include semiconductors with high spin-orbit coupling such as InAs on GaSb, and InAs on InP which are coupled to a s-wave

MBE grown material based upon hybrid semiconductor-superconductor has generated a lot of interest recently due to the possibility that it allows for the emergence of Majorana

icant step toward generating MZMs with InSb 2DEGs.

 involuntarily observed, demonstrating phase coherent transport. These measurements reveal the high quality of these structures. This generic platform will open new applications in quantum

We present structural characterization of superconducting Al layers on MZM structures.

MBE grown material based upon hybrid semiconductor-superconductor has generated a lot of interest recently due to the possibility that it allows for the emergence of Majorana

Here we will show how the growth of thin epitaxial aluminum is extremely sensitive to temperature. Deposition or working at T>0°C causes many grains to form or the film to ball

It is essential to avoid Al-Sb intermixing [2] and to measure the first evidences of coupling between Al and InSb 2DEGs. These results are

While InSb nanowires epitaxially coupled to Al have already experimentally demonstrate their ability to generate MZMs [1], the realization of planar superconductor-

vicinity of the Al-InSb interface have been required to prevent Al-Sb intermixing [2] and to measure the first evidences of coupling between Al and InSb 2DEGs. These results are

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and their signature conductance peaks [2] will be observed directly in a planar geometry with near-perfect topological protection. This experimental realization is a crucial step

and more complex networks with top-down lithography and gating. We will first report on the growth developments of InSb two-dimensional electronic layer (2DEGs) on GaAs (100) substrates. These structures exhibit high carrier mobility up to 10^6 cm²/Vs. The direct coupling between InSb 2DEGs and Al layers opens new possibilities for realizing topological quantum computing devices. For instance, the coherent manipulation of Majorana zero modes in Al-InSb hybrid structures could be achieved through the exchange of a topological superconductor. Relevant material platforms for MZM based devices include semiconductors with high spin-orbit coupling such as InAs on GaSb, and InAs on InP which are coupled to a s-wave superconductor that shows 2e periodicity in a closed system. Thin aluminum films, <70nm, meet these requirements and have been shown to have a high critical in-plane magnetic field of Bc2 of ~1.5 T.

MBE grown material based upon hybrid semiconductor-superconductor has generated a lot of interest recently due to the possibility that it allows for the emergence of Majorana Zero Modes (MZMs) which may offer topological protection for quantum computing. [1]

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The in-situ epitaxial deposition of Al on top of these InSb 2DEGs will also be reported. Careful optimization of the Al deposition conditions and of the heterostructure design at the vicinity of the Al-InSb interface have been required to prevent Al-InSb intermixing [2] and to measure the first evidences of coupling between Al and InSb 2DEGs. These results are an important step toward generating MZMs with InSb 2DEGs.

Here we will show how the growth of thin epitaxial aluminum is extremely sensitive to temperature. Deposition or working at T>0°C causes many grains to form or the film to ball up while deposition of Al films at T<77K shows good morphology but not the requisite crystallinity. Thin films, <10nm, deposited within the good temperature window on planar substrate, show structure which matches the semiconductor and has two distinct in-plane orientations, both are (111) in plane. This Al-InAs hybrid system shows an induced gap >200µeV. We present structural characterization of superconducting Al layers on MZM structures.


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With its high-γ factor, strong spin-orbit coupling and low effective mass, InSb is a candidate to host Majorana Zero Modes (MZMs) when coupled to a s-wave superconductor. While InSb nanowires epitaxially coupled to Al have already experimentally demonstrated their ability to generate MZMs [1], the realization of planar superconductor-

semiconductor hybrid heterostructures is required to improve scalability and fabricate more and more complex networks with top-down lithography and gating. We will first report on the growth developments of InSb two-dimensional electron layer (2DEGs) on GaAs (100) substrates. These structures exhibit high carrier mobility up to 190,000 cm²/Vs and have provided the first observation of induced superconductivity in InSb 2DEGs using Josephson junctions made with ex-situ deposited NbTiN electrodes.

The in-situ epitaxial deposition of Al on top of these InSb 2DEGs will also be reported. Careful optimization of the Al deposition conditions and of the heterostructure design at the vicinity of the Al-InSb interface have been required to prevent Al-InSb intermixing [2] and to measure the first evidences of coupling between Al and InSb 2DEGs. These results are an important step toward generating MZMs with InSb 2DEGs.

Here we will show how the growth of thin epitaxial aluminum is extremely sensitive to temperature. Deposition or working at T>0°C causes many grains to form or the film to ball up while deposition of Al films at T<77K shows good morphology but not the requisite crystallinity. Thin films, <10nm, deposited within the good temperature window on planar substrate, show structure which matches the semiconductor and has two distinct in-plane orientations, both are (111) in plane. This Al-InAs hybrid system shows an induced gap >200µeV. We present structural characterization of superconducting Al layers on MZM structures.


Epitaxial Al-InAs structures are prime candidates for tunable superconducting qubits, the so-called “gatemon” where the Josephson energy can be tuned in-situ with an applied electric field to an InGaAs Josephson junction, eliminating the need for flux tuning in superconducting qubits [1]. Here we have characterized microwave cavity modes needed for coupling to superconducting gatemon qubits. We present resonator quality factors for a fixed design on various levels of the buffer layers used as substrates. We make a comparison to bare InP and Si to establish a comparative baseline. We study the relationship of anharmonicity in gatemon qubits to interface transparency in the Superconductor-Semiconductor structure.


We acknowledge support from the US Army Office of Research, ARO: W911NF-18-1-0067

4:45 PM QN06.02.09

Semiconductor/Ferromagnetic Insulator InAs/EuS Epitaxy Yu Liu and Peter Krogstrup; University of Copenhagen, Copenhagen, Denmark.

Material development holds promise as the basis of topological quantum computing with Majorana fermions. These quasiparticles have been predicted at ends of semiconductor nanowires coupled to conventional superconductors [1-2]. These predictions were followed by a series of experiments providing transport signatures consistent with these theories [3-4]. These early measurements suffered from soft induced superconducting gap, which later was significantly improved by growing epitaxial semiconductor-superconductor (SE-SU) nanowires [5-6]. In order to reach the topological phase, an external magnetic field needed to lift the spin degeneracy in these SE-SU systems, which brings an even larger challenge for achieving scalable solutions. Therefore, in order to integrate and scale up a topological quantum plane, materials that are intrinsically topological (without the need for an external applied field) would be highly preferable. Composite tri-crystals using ferromagnetic insulators (FMI) in close proximity to the SE-SU structure have been proposed as a solution to lift the spin degeneracy [7], where the Zeeman splitting could be induced by the exchange field from the FMI.

In this work, we study hybrid SE-FMI epitaxy of EuS on different InAs crystallographic platforms as the initial basis of tri-crystal SE-SU-FMI NW systems. These SE-FMI systems prove to fulfill key requirements for the realization of topological quantum computing material without need of large external magnetic field:
1. The EuS thin film grown on (100) Zn Blende InAs surface is fully coherent.
2. An exchange field exists by inducing magnetic moments into InAs of about 2 nm.
3. InAs/EuS NWs have strong shape-derived single magnetic domains along the NW length with Curie temperature of 19 K.

The results not only show the InAs/EuS hybrid crystals as promising candidates for topological quantum computing, but also confirm EuS as a promising FMI for various spin applications.

Aluminum oxide (AlO$_x$) is extensively utilized as the tunnel barrier or the gate dielectric in quantum information (QI) devices. However, AlO$_x$ often has a wide distribution of defects originating from the nonequilibrium structure, which affects the electrical stability of devices containing AlO$_x$. One manifestation of the device instability that is often observed on single-electron transistors (SETs) is a time instability named charge offset drift, which is a nanoscale probe of sub-1 e charged defect motion. In this work, we present excellent long-term charge offset stability (very small charge offset drift) measured from two types of SETs containing AlO$_x$: all-metallic AlO$_x$ tunnel junction-based devices and tunable barrier silicon-metal-oxide-semiconductor (MOS) devices. For the all-metallic devices, plasma-oxidized AlO$_x$ is used as the tunnel barrier and the device fine structure is fabricated by double-angle e-beam evaporation. The long-term charge offset stability measured from these devices are better than any other reported metallic SETs, with very small linear charge offset drift of < 0.1 e and standard deviation of < 0.01 e over 7.5 days. For the silicon MOS devices, thermally-oxidized AlO$_x$ is used to electrically isolate overlapping layers of aluminum gates and the devices are made on a silicon-on-insulator (SOI) substrate. These devices display a linear drift of < 0.07 e and standard deviation of < 0.02 e over 7 days. The above results demonstrate good electrical stability using AlO$_x$, which opens the future for large-scale device integration and improving qubit performance.

**QN06.03.04**

**Defects in Wide Band Gap Semiconductors for Quantum Computing**

*Panna Biswal* 1,2; Renu Choudhary 3, Bicai Pan 4 and Durga Paudyal 5; 1 Iowa State University, Ames, Iowa, United States; 2DMSE, Ames Laboratory, Ames, Iowa, United States; 3University of Science and Technology of China, Hefei, China.

Many novel materials are being actively considered for quantum information science and for realizing high performance qubit operation at room temperature. It is known that deep defects in wide-band gap semiconductors can have spin states and long coherence times suitable for qubit operation. We theoretically investigate from ab-initio density functional theory (DFT) that the defect states in the hexagonal silicon carbide (4H-SiC) and boron nitride are potential qubit materials. The DFT supercell calculations were performed with the local-orbital and pseudopotential methods utilizing hybrid exchange-correlation functionals. Dv-vacancies in SiC supercells yielded defect levels in the gap consisting of closely spaced doublet just above the valence band edge, and higher levels in the band gap. The divacancy with a spin state of 1 is charge neutral. The divacancy is characterized by C-dangling bonds and a Si-dangling bond. Jahn-Teller distortions and formation energies as a function of the Fermi level will be discussed. Single photon interactions with these defect levels will be discussed. In contrast, the anti-site defects where C, Si are interchanged have high formation energies of 5.4 eV and have just a single shallow defect level close to the valence band edge, with no spin. We will compare results including the defect levels from both the electronic structure approaches. Simulations for BN will be compared with those of SiC. We will also discuss prototypical (s,p) electron systems within group IIIA-IVA-VA elements and possible rare earth doped semiconductors for qubit operation.

**QN06.03.05**

**Coherent Single Photon Emission from Colloidal Lead Halide Perovskite Quantum Dots**

*Hendrik Uzat*, Weiwei Sun, Alex Kaplan, Franziska Krieg 1, Matthias Gintereder 1, Boris Spokony 1, Nathan Klein 1, Katherine Shulenberger 1, Colin Perkins 1, Maksum V. Kovalenko 3 and Moungi Bawendi 1; 1 Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Institute of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zurich, Zurich, Switzerland; 3Laboratory for Thin Films and Photovoltaics, Empa–Swiss Federal Laboratories for Materials Science and Technology, Duesseldorf, Switzerland.

Chemically prepared colloidal semiconductor quantum dots, most notably based on CdSe, have long been proposed as scalable and color-tunable single emitters for optical quantum information technologies. They have, however, suffered from prohibitively incoherent and unstable emission characterized by pronounced spectral diffusion and fluorescence intermittency at low temperatures.[1]

We now demonstrate that novel colloidal lead halide perovskite quantum dots (PQDs)[2,3] display a real utility as practical quantum emitters with unity emission efficiency and color-tunability over the entire visible spectral range. We show that a unique combination of long optical coherence times (T2 ~ 20 ps) and high oscillator strength (radiative lifetime T1 ~ 210 ps) at low temperatures, renders the emission of PQDs highly coherent. 1,4 Indeed, the degree of coherence (T2/T1) already approaches values of self-assembled III-V quantum dots – even without cavity integration. Using photon-correlation-Fourier spectroscopy we furthermore demonstrate that the spectral stability of PQDs is drastically improved compared to established quantum dots and is already comparable to some nitrogen-vacancy centers in diamond. We attribute this superior spectral stability to the absence of surface-trap states in lead halide perovskite semiconductors. Together with the observed high single photon emission purity (g2(0) < 0.04) and high fraction of coherently emitted photons (~0.85), our results suggest that PQDs – unlike any other chemically-made semiconductor quantum dot material – can be explored as sources of indistinguishable single photons and entangled photon pairs for quantum information technologies. We present our ongoing synthetic efforts to further increase the optical coherence and reduce the inhomogeneous broadening, which is already as small as for typical self-assembled III-V quantum dots.

Our results suggest that lead halide perovskites – with their high defect tolerance and bright lowest-lying exciton state [5] – are promising semiconductors for the scalable production of quantum emitters with highly coherent emission that can be processed onto virtually any substrate and that benefit from the integration with hybrid nano-photonic components that has been demonstrated for colloidal materials. Unlike defect centers in diamond, PQDs can be rationally optimized via the structure of the quantum dot, a research effort that will require input from the quantum photonics and colloidal chemistry community.

Realization of Hybrid Superconductor-Semiconductor Systems by Homoepitaxial Growth of Non-Equilibrium P-Doped Si(111) Mehdi Hatéfipour\textsuperscript{1}, Kasra Sardashi\textsuperscript{1,2}, Kaushini S. Wickramasinghe\textsuperscript{1}, Tri Nguyen\textsuperscript{1}, William Mayer\textsuperscript{1}, Joseph O. Yuan\textsuperscript{1} and Javad Shabani\textsuperscript{1}; 1Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia; 2Department of Science and Math, Fashion Institute of Technology, New York, New York, United States; 3Center for Nanoscale Materials, Lemont, Illinois, United States; 4Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

To fulfill the long-term vision of reliable quantum computation, the ideal hybrid platform allows quantum information to be processed, stored and transmitted on the same materials system [1]. Silicon can be a promising candidate for fault-tolerant hybrid quantum systems due to its multifunctionality and reliability as well as long coherence times [2]. Superconducting Si could provide a viable pathway for the realization of Si qubit circuits, by forming homogeneous Superconductor–Semiconductor–SC Josephson junctions. In this work, non-equilibrium p-doping of Si thin-films by homoeptaxial growth of Ga-rich Si on Si(111) is studied. MBE approaches to form this superconductor–semiconductor–SC junctions were fabricated and characterized. The p-doping levels and carrier concentrations were determined by temperature-dependent resistivity (\(\rho\)–T) measurements in 4-point van der Pauw and on Hall bars. Upon increase in Ga incorporation, \(\rho\)–T characteristics of the p-doped films transitioned from insulating to quasi-reentrant superconductivity with \(R_{\text{in}}/R_0\) of 0.82–0.89. Based on the known theories, primary growth mechanisms and strategies to go beyond the quasi-reentrant regime will be discussed.

This work is supported by the US Air Force Office of Scientific Research Young Investigator Award, FA9550-16-1-0348.


9:15 AM QN06.04.03
Characterization of Er Defect Centers in Epitaxially Grown Er Doped Y2O3 Manish Kumar K. Singh\textsuperscript{1}, Khan Alam\textsuperscript{2,4}, Tijana Rajh\textsuperscript{2}, Tian Zhong\textsuperscript{1,2} and Supratik Guha\textsuperscript{1,2,1}; 1University of Chicago, Chicago, Illinois, United States; 2Argonne National Laboratory, Lemont, Illinois, United States; 3Center for Nanoscale Materials, Lemont, Illinois, United States; 4Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

Erbium, with optical transition in the 1.5um band is one of the attractive REI candidates for optical quantum memory. Recent studies have, overcome unique challenges that erbium presents and have shown coherence times exceeding 1 second in \(^{166}\)Er. The coherence properties of REI are critically dependent on the host crystals, and methods of incorporating REI into the host structures play an important role as structural defects and impurities determine the local environment of the ions, which is an important factor contributing to linebroadening mechanisms.

Rare-earth oxides with low or no nuclear spin, such as CeO2 and Y2O3 are preferred host material for REI. The ability to tailor the properties of these systems on demand will be a powerful tool for quantum information applications. Molecular beam epitaxy (MBE) allows us to grow single crystal thin epitaxial films of certain RE oxides, and also enables precise control over the doping concentrations.

In this study Er-doped Y2O3 thin films were grown epitaxially on Si(111) using molecular beam epitaxy (MBE). Electron paramagnetic resonance (EPR) spectra of these samples show angular dependence of Er signal indicating crystalline quality of the host material. The site occupancy and crystalline environment of Er defect centers were studied by monitoring interpatter between carrier concentration, film thickness and angular dependence of Er signal. The samples were grown using an oxygen plasma source and the EPR linewidth indicates an inverse dependence on the oxygen pressure during growth. PLE measurements show that Er atoms are present in the C2 and C3 sites substituting for Y. Further, preliminary results for optical linewidth parallel the dependence seen in EPR linewidth. In addition, post-growth anneal in an oxygen atmosphere shows improvement in the EPR and PLE signal intensity and the linewidth.

9:30 AM QN06.04.04
Hybrid Superconducting Circuits Made with Graphene-Based van der Waals Heterostructures I-Jan Wang\textsuperscript{1}, Daniel Rodan-LeGrain\textsuperscript{2}, Charlotte Böttcher\textsuperscript{1}, Landry Bretheau\textsuperscript{1}, Daniel L. Campbell\textsuperscript{1}, Bharath Kannan\textsuperscript{1,3}, David Kim\textsuperscript{4}, Morten Kjaergaard\textsuperscript{1}, Philip Krantz\textsuperscript{1}, Gabriel O. Samach\textsuperscript{5,6}, Fei Yan\textsuperscript{1}, Jonilyn Yoder\textsuperscript{7}, Kenji Watanabe\textsuperscript{2}, Takashi Taniguchi\textsuperscript{7}, Terry P. Orlando\textsuperscript{1,4}, Simon Gustavsson\textsuperscript{1}, Pablo Jarillo-Herrero\textsuperscript{2} and William D. Oliver\textsuperscript{1,3}; 1RLE, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 2Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 3Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, France; 4Physics, Harvard University, Cambridge, Massachusetts, United States; 5Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 6Lincoln Lab, Massachusetts Institute of Technology, Lexington, Massachusetts, United States; 7Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Japan.

Temporal quantum coherence and control is foundational to the science and engineering of quantum systems. Improving such coherent characteristics in quantum systems, a key to realizing extensible quantum computing schemes, may be accomplished in part by introducing new materials with superior properties.

Van der Waals (vdW) materials - a family of layered crystals including semi-metals, insulators, semiconductors, ferromagnetic materials, superconductors, and topological insulators - can be assembled in specific arrangements to create new electronic devices called vdW heterostructures. The extraordinary and versatile electronic properties of these heterostructures, in combination with their epitaxial precision, make vdW-based devices a promising alternative for constructing key elements of novel solid-state quantum computing platforms.

We demonstrate quantum coherent control of a superconducting circuit incorporating graphene-based vdW heterostructures. We show that this device can be operated as a voltage-tunable transmon qubit, whose spectrum reflects the unique electronic properties of massless Dirac fermions traveling ballistically. In addition to the potential for advancing extensible quantum computing technology, our results represent a new approach to studying vdW materials using microwave photons in coherent quantum circuits. (arXiv:1809.05215 (2018))

This research was funded in part by the ARO grant No. W911NF-17-S-0001, and by the Department of Defense via MIT Lincoln Laboratory under AF Contract No. FA8721-05-C-0002. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the U.S. Government.

10:00 AM BREAK

SESSION QN06.05: Superconductors I
Session Chairs: Javad Shabani and I-Jan Wang
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 127 B

10:30 AM QN06.05.01
A Density-Functional Theory Study on Al/AlO\textsubscript{x}/Al Tunneling Junction Chang-Fun Kim, Keith G. Ray and Vincenzo Lordi; Lawrence Livermore National Laboratory, West Lafayette, Indiana, United States.

The aluminum oxide tunnel junction is one of the key components in most superconducting qubit devices. We use density functional theory to investigate the microscopic details of the junction. By using ab-initio molecular dynamics and rigorous static ground state calculations, we accurately model the details of the discrete transition of electronic structure.
across the tunneling interface. Significantly, the aluminum-oxygen coordination is found to vary across the junction, creating irregular potential field that is not well described by the conventional and popular models such as the Landauer–Büttiker method in a constant potential approximation. We aim to provide the atomistic, electronic details of this unique interface as described by the first-principles density functional theory to explore its non-idealities and potential sources of dissipation and loss. The ab-initio result provides a correction to a previous study on the atomic coordinations based on the reverse Monte Carlo method. The calculated work function of the oxide film of the junction was 6.2 eV compared to 4.0 eV for the aluminum metal. The atomic dipole moments are calculated using the Bader’s atoms-in-molecules method, describing the dielectric property of the junction in a microscopic detail. The defect formation energies in the vicinity of the junction interface are calculated by the nudged elastic band method. The ab-initio calculations present further research opportunities to incorporate atomistic details into the device scale simulations of the superconducting qubits. Prepared by LLNL under Contract DE-AC52-07NA27344.)

10:45 AM QN06.05.02
Superconductive Rhenium Thin Films Electrodeposited from Water-in-Salt Electrolytes Qiang Huang1, Yang Hu2, William Sides2, David Pappas1 and Tyler Lyons1; 1National Institute of Standards and Technology, Boulder, Colorado, United States; 2Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, Alabama, United States.

Electrodeposition has been used widely in the fabrication of microdevice and circuits because of the low cost, fast deposition rate, and, more importantly, the ease of scale-up. Electrodeposited superconductive films are of interest for cryogenic quantum devices as it avoids thermal perturbation resulted from the electrical heat. Such films are particularly of interest if the critical temperature (Tc) is above 4.2 K, which can be easily achieved with liquid helium. Recently, electrodeposited rhenium was demonstrated to show a critical temperature of about 6 K, representing a significant increase from its intrinsic 1.7 K[1]. However, electrodeposition of rhenium requires an acidic electrolyte, where significant hydrogen evolution is inevitable and causes inclusion of hydrogen and highly stressed or even cracked films. On the other hand, a so-called hydration layer forms during the dissolution of salts in water. Such hydration process requires and “consumes” water molecules. When an electrolyte contains a superhigh concentration of supporting salts, for example, alkali metal salts, the hydration of such salts can deplete the free water molecules in the aqueous electrolyte and significantly mitigates the evolution of hydrogen[2,3]. This paper presents a new electrodeposition method to synthesize superconductive rhenium films using water-in-LiCl electrolyte. A limiting current density emerged upon the addition of 5 M LiCl into an acidic Re electrolyte. This lowered hydrogen evolution reaction not only limited the voltage drop due to the high current and solution resistance, but also enabled electrochemical treatments at more negative potentials. An improved film morphology was observed with a suppressed hydrogen evolution currents when the water-in-salt electrolyte was used. A critical temperature of 6 K for as-deposited rhenium film was achieved and a decrease of Tc was observed for the films upon annealing at beyond 150 C. The details of chemical uniformity, grain structures, and Tc of such Re films will be presented. In addition, attempts to electrodeposited Re alloys with this water-in-LiCl electrolyte will be discussed as well.

REFERENCES

11:00 AM QN06.05.03
Reducing Two-Level State Defects in Superconducting Resonators and Qubits Matteo Mariantoni, Jérémie H. Béjanin, Carolyn T. Earnest and Evan A. Peters; University of Waterloo, Waterloo, Ontario, Canada.

Practical quantum computers are closer to reality than ever before. Superconducting qubits, for example, have already been integrated in arrays of ~50 qubits and can be further integrated. However, dissipation phenomena due to imperfect materials largely limit the time a qubit can store quantum information. Qubit dissipation or decoherence is mainly due to quasiparticles, flux noise, and two-level state (TLS) defects. The last are material imperfections hosted in oxidized films in proximity of on-chip superconducting devices. In this talk, we focus on TLS loss and investigate different strategies to reduce their impact on the quality of superconducting resonators and qubits. First, we fabricate and characterize coplanar waveguide resonators made from aluminum thin films deposited on silicon substrates. We perform three different substrate surface treatments prior to aluminum deposition: One chemical treatment based on a hydrofluoric acid clean; one physical treatment consisting of a thermal annealing at 880 °C in high vacuum; one combined treatment comprising both the chemical and the physical treatments. We characterize the fabricated samples through cross-sectional tunneling electron microscopy, acquiring electron energy loss spectroscopy maps of the samples’ cross sections. We analyze the effects of the various substrate treatments on the roughness of the silicon surface by means of atomic force microscopy surface morphology mapping. We study the quality of the resonators by means of microwave measurements in the quantum regime and find that both surface treatments independently improve the resonator’s intrinsic quality factor and that the highest quality factor is obtained for the combined treatment, Q∼0.8 million.

We then employ similar fabrication methods as for resonators to implement superconducting Xmon transmon qubits. We characterize qubit decoherence finding energy relaxation times on the order of ~15 μs for fully flux tunable Xmons. We study the qubits by implementing one-qubit gates, while biasing the qubits using our three-dimensional wiring method, the quantum socket. Lastly, we present the blueprints of a new type of superconducting qubit, the “pocketmon” transmon qubit. This type of qubit is a variant of the Xmon, where the qubit capacitor is realized as an almost ideal parallel-plate capacitor with vacuum as dielectric. To implement the pocketmon qubit we develop a thermocompression bonding technology, which makes it possible to fabricate multi-chip devices. The qubit is comprised of two silicon chips: The base and the cap chip. A meandered aluminum inductor and the bottom square aluminum plate of a capacitor are patterned on the base chip; the inductor is connected to a common aluminum ground plane on one end and to the capacitor through an aluminum lead on the other end. The cap chip is etched to form vacuum pockets in correspondence to the inductor, capacitor, and lead, with an aluminum square plate and a common ground plane matching those on the base chip; the top capacitor plate is connected to ground by way of an aluminum lead. The common ground plane is coated with an indium film used to bond the base and cap chip. The distance between the two capacitor plates is set to be ~10 μm. The aluminum films used to realize the capacitor plates are characterized by an atomic dipole moments are calculated using the Bader’s atoms-in-molecules method, describing the dielectric property of the junction in a microscopic detail. The diffusion property across the junction interface are assessed by the nudged elastic band method. The ab-initio calculations present further research opportunities to incorporate atomistic details into the device scale simulations of the superconducting qubits. Prepared by LLNL under Contract DE-AC52-07NA27344.)

This research was undertaken thanks in part to funding from the Canada First Research Excellence Fund (CFREF) and the Discovery and Research Tools and Instruments Grant Programs of the Natural Sciences and Engineering Research Council of Canada (NSERC).

11:15 AM QN06.05.04
MBE Grown Nitride Heterostructures for Superconducting Quantum Circuits Christopher Richardson1, Ashish Alexander1 and Chris Weddle2; 1University of Maryland, College Park, Maryland, United States; 2Laboratory for Physical Sciences, College Park, Maryland, United States.

Low microwave loss superconducting circuit components are a necessity of fabricating high-fidelity superconducting qubits. Accordingly, significant research has focused on making high-quality planar resonators from elemental and nitride superconductors. Josephson junctions are the nonlinear component of superconducting qubits, that also need to be high performance. Interestingly, superconducting qubits all use Josephson junctions fabricated from aluminum and aluminum oxide using the double angle evaporation process. Details of this alternative design will be presented.

Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow binary and ternary niobium titanium nitride alloys (Nb,Ti,N) and wide bandgap nitride (AIN) superconductors. This combination of nitride materials provides sufficient degrees of freedom that synthesis of an epitaxial Josephson junction may be possible. Using a structure first approach to design optimization, the structural, surface topology, chemical characteristics, and superconducting critical temperature of these films are used for optimization of the growth conditions before resonators are fabricated and tested. Initial growth results of nitride superconductors exhibit significant atomic interaction of the deposited adatoms and silicon substrates. Both amorphous interfacial layers, and significant diffusion of silicon during the formation of silicides are observed. Interpretation of the observed structures and impact on the superconducting properties will be assessed.
The outstanding progress in experimental quantum computing with superconducting Josephson-junction based qubits over the past few decades has pushed coherence times many orders of magnitude above that of the first measured. We are also in the midst of scaling towards complex architectures of multi-qubit processors where maintaining very low gate error rates at the limits supported by coherence times is extremely important. Here we will review some of the critical materials and device challenges for superconducting qubits from the perspective of improved coherence and improved error rates. Furthermore, we will discuss traditional validation and verification techniques, while also discussing alternatives to benchmark the performance of small quantum processors for near-term applications.

Superconducting quantum computing architectures rely on resonators and qubits with coherence lifetimes that are limited by two-level systems (TLS) present in bulk and interfacial dielectrics. Understanding this source of loss is critical to improving performance in superconducting circuits. However, few techniques exist for characterizing material issues associated with loss in the single photon regime by simply removing interfaces near qubits. I will introduce the mechanism of energy loss due to two-level system and share results of error rates at the limits supported by coherence times is extremely important. Here we will review some of the critical materials and device challenges for superconducting qubits from the perspective of improved coherence and improved error rates. Furthermore, we will discuss traditional validation and verification techniques, while also discussing alternatives to benchmark the performance of small quantum processors for near-term applications.


Two-level state (TLS) loss in dielectric materials and interfaces remains at the forefront of materials research in quantum information science. Due to a lack of defects and decreased disorder, crystalline films grown epitaxially in an ultrahigh vacuum environment are thought to have a reduced TLS concentration and thus lower loss at millikelvin temperatures and single photon powers [1]. In this work, we demonstrate a method of sensitive and accurate TLS loss measurement by measuring a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer. The deposition of the trilayer prior to fabrication increases control over the metal-dielectric interfaces, and the generalized fabrication process allows straightforward comparison of dielectrics that are of interest to quantum computing. We extract the dielectric loss by comparing to coplanar waveguide resonators and lumped element resonators with interdigitated capacitors. This method is designed to compare dielectric loss in both epitaxial and non-epitaxial trilayers.


Two-level state (TLS) loss in dielectric materials and interfaces remains at the forefront of materials research in quantum information science. Due to a lack of defects and decreased disorder, crystalline films grown epitaxially in an ultrahigh vacuum environment are thought to have a reduced TLS concentration and thus lower loss at millikelvin temperatures and single photon powers [1]. In this work, we demonstrate a method of sensitive and accurate TLS loss measurement by measuring a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer. The deposition of the trilayer prior to fabrication increases control over the metal-dielectric interfaces, and the generalized fabrication process allows straightforward comparison of dielectrics that are of interest to quantum computing. We extract the dielectric loss by comparing to coplanar waveguide resonators and lumped element resonators with interdigitated capacitors. This method is designed to compare dielectric loss in both epitaxial and non-epitaxial trilayers.

Superconducting quantum computing architectures rely on resonators and qubits with coherence lifetimes that are limited by two-level systems (TLS) present in bulk and interfacial dielectrics. Understanding this source of loss is critical to improving performance in superconducting circuits. However, few techniques exist for characterizing material losses under conditions relevant to superconducting quantum circuit operation. In this work, we present a method for quantifying the TLS losses of different bulk and interfacial dielectrics present in superconducting coplanar waveguide (CPW) resonators. By combining statistical characterization of sets of specifically designed CPW resonators on isotropically etched silicon substrates with detailed electromagnetic modeling, we determine the separate loss contributions from individual material interfaces and bulk dielectrics. Additionally, we report on progress towards applying this technique to characterize and improve qubit losses. In general, this technique provides an effective method for assessing superconducting qubit materials in order to guide targeted improvements to qubits, resonators, and their superconducting fabrication processes.

This material is based upon work supported in part by the Intelligence Advanced Research Projects Activity (IARPA) and in part by the Department of Defense under Air Force Contract No. FA8721-05-C-0002 and/or FA8702-15-D-0001. Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of IARPA, the Department of Defense, or the US Government.

Searching for the Origins of Loss in Superconducting Qubits

Two-level state (TLS) loss in dielectric materials and interfaces remains at the forefront of materials research in quantum information science. Due to a lack of defects and decreased disorder, crystalline films grown epitaxially in an ultrahigh vacuum environment are thought to have a reduced TLS concentration and thus lower loss at millikelvin temperatures and single photon powers [1]. In this work, we demonstrate a method of sensitive and accurate TLS loss measurement by measuring a lumped element resonator fabricated from a superconductor-dielectric-superconductor trilayer. The deposition of the trilayer prior to fabrication increases control over the metal-dielectric interfaces, and the generalized fabrication process allows straightforward comparison of dielectrics that are of interest to quantum computing. We extract the dielectric loss by comparing to coplanar waveguide resonators and lumped element resonators with interdigitated capacitors. This method is designed to compare dielectric loss in both epitaxial and non-epitaxial trilayers.

participation model, the measured quality factor of the resonators can be related to the loss tangent (\(\tan(\delta)\)) associated with TLSs by \(\sum p_i \tan(\delta) = Q_{TLS}^\text{i} \) where \(p_i\) is the participation ratio of the electric field which is the fraction of the total electric energy stored at each interface.

In this study, the role of different chemical species at various interfaces of the coplanar waveguide resonators are investigated. Quarter-wavelength coplanar waveguide resonators are fabricated from MBE grown aluminum (Al) on silicon (Si (111)) wafers. Resonators are wet-etching to ensure that the devices are as identical as possible. Devices are packaged and measured consistently to reduce any other sources of variation in the measured quality factor. Variations in the surfaces are introduced by distinct treatments on Si and Al surfaces that allow comparison of interfaces with different incorporation values of oxygen and nitrogen. These surface treatments also modify the structural properties of the overgrown Al showing polycrystalline, twinned single crystal, and pure single crystal Al films.

These treatments of the Si and Al surfaces impact the measured quality factor. The low loss devices have single photon internal quality factor near 800k. The measured data along with the simulated participation ratio is used to calculate the relative loss tangent across the tested interfaces. The relation between the calculated loss tangent and the various chemical species present at interfaces will also be explored.

4:00 PM QN06.06.06


A continuous taper can be engineered between two transmission lines of different characteristic impedance to reduce reflection of the signal that propagates from one line to the other. There are a number of taper designs presented in the literature that achieve this goal. [1,2] These designs assume impedance mismatch of the two lines is sufficiently small that voltage reflections within the taper also can be considered small. Here we extend the theory of the optimal lossless impedance taper of [2], allowing for impedance mismatch and voltage reflection of arbitrary magnitude. We apply our extended theory to the optimal design of taper for the two use cases of (i) an unavoidably large impedance mismatch between transmission lines and (ii) a narrow notch filter corresponding to a specific range of frequencies of bandpass. We also apply our theory to a proposed design of on-chip Purcell filter, which can be used in the fast readout of superconducting transmon and Xmon qubits, for example.

* This work was supported by the NIST Quantum Initiative. RPE acknowledges grant 70NANB17H033 from the US Department of Commerce, NIST.


4:15 PM QN06.06.07

The Role of Fields, 2D Stacking and Long-Range Order in the Search of Majorana Fermions in a Honeycomb Kitaev Candidate Arnab Banerjee1, Christian Balz1, Paula Kelley2, Craig Bridges1, Jiaqi Yang1, Yaohua Liu1, David Mandrus1 and Stephen Nagler1; 1Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; 2Material Science and Engineering, The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

The 2D Kitaev model on a honeycomb lattice predicts a special quantum spin liquid (QSL) ground state with excitations resembling Majorana Fermions and gauge flux excitations. These emergent features are exciting prospects to both basic physics and applications towards technologies for topologically protected quantum qubits. Our past range of experiments on the 2D magnetic Mott insulator alpha-RuCl3, which has honeycomb layers held together with weak van-der-Waals interactions, have revealed a continuum of fractionalized excitations resembling predictions from Majorana Fermions. In a 8 T magnetic field, the long-range order vanishes and the continuum becomes gapless, supporting a state where direct evidence of non-Abelian excitations can be measured. Interestingly, within this 8 T phase, recent thermal Hall effect measurements have revealed 1/2-quantized chiral edge states reminiscent of free Majorana Fermions stable to 5 K, producing a lot of excitement in the community. In this talk, I will describe our recent neutron experiments on the role of the 3D magnetic long-range order and the nature of the 2D stacking, which is critical to understand this material and its phases. Our result point to the hierarchy of the 2D (within a 2D layer) and 3D interactions (between the 2D layers) in the Hamiltonian which is responsible for the physics observed. I will describe the present and future endeavors to complete the understanding of the phase diagram of this material, as well as on how to stabilize the phase where these excitations are observed.

SESSION QN06.07: Foundation Materials Science for QIS
Session Chairs: Jeremy Levy and Tzu-Ming Lu
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 127 B

8:30 AM QN06.07.01

Electrical Transport Measurements of Quantum Structures with Atomically Precise Probes Markus K. Maier and Brandon Giles, Scienta Omicron GmbH, Denver, Colorado, United States.

A major challenge in the development of novel devices in molecular and atomic scale electronics and specifically in QBits for Quantum Information Processing (QIP) is their interconnection with larger scaled electrical circuits. Local electrical probing by multiple probes with atomic precision can significantly improve efficiency in analyzing electrical properties of individual structures without the need of a full electrical integration. The LT NANOPROBE merges a SEM navigated 4-probe electrical transport measurement system with four individual high stability SPM’s with precision in the pm range. This exact stability allows for atomic resolution in STM and nc-AFM (QPlus) and expands applications towards the creation of atomically precise structures and their direct analysis by electrical transport measurements and SPM based spectroscopy methods.

The system - including simultaneous SEM probe navigation - is operated near thermal equilibrium at T< 5K and has been developed towards an extremely low thermal drift, which is the most important ingredient to allow for enough measurement time on atomic structures, a precision regime that is virtually inaccessible at room temperature. We will present the technical concept and measurements that prove the performance level of the instrument, specifically low thermal drift and pm stability. As an exciting application, we will refer to atomic scale lateral transport measurements on dangling bond dimer rows created on hydrogenated Ge(001), in which probes are as close together as 30nm and positioned for transport measurements from atom to atom.

We will also show the newest technology improvements, such as high frequency capabilities and optical access for pumped probe experiments. Future technology challenges as well as applications and scientific drivers for this type of scientific instrumentation will be discussed.

8:45 AM *QN06.07.02

First Principles Atomistic Modeling of Decoherence Sources in Qubit Devices Vincenzo Lordi; Lawrence Livermore National Laboratory, Livermore, California, United States.

Understanding the detailed materials origins of decoherence in qubit devices will enable rational design of improved devices and fabrication processes for practical quantum information processing. We utilize first principles materials simulations to study a range of possible coherence-limiting defects and materials properties at the atomic scale. Examples will be presented for superconducting qubits, ion trap qubits, and silicon/silicon-germanium quantum dot qubits.

Specifically, we will review our recent work in the computational search for sources of flux and dielectric noise in superconducting qubits, including paramagnetic surface impurities, grain boundary effects, the atomic structure of Josephson junction dielectric layers, and the dielectric response of interface features. Many of these atomic features are associated with spurious two-level fluctuators that couple to the qubit and cause decoherence. For ion traps, possible sources of anomalous heating associated with electrode materials and surface impurities are studied with atomistic simulations. The phenomenon of anomalous motional heating of the trapped ion is a major limiting factor of the coherence time for surface ion trap devices. Various levels of detail are used to model the surfaces and impurities realistically. Finally, we will describe studies of dangling bond defects in insulating layers of silicon and silicon-germanium quantum dot devices as a possible source of charge noise in those devices. Prepared by LLNL under Contract DE-AC52-07NA27344.
Cooled samples to cryogenic temperatures is common for quantum materials and quantum information devices. Effective cooling requires adequate thermal conduction pathways between the cooling stage and the sample. A three-tiered structure of CTE mismatch (sample/mounting material/stage) is studied. Silicon wafers are good standard reference samples widely used across thin film research, are flat and mirror-like surfaces that will reflect a laser signal. The curvature of a Si wafer sample is measured in real time as a function of temperature. A projected pattern of laser spots is reflected from a piece of Si wafer that is mounted to a stage in a cryostat. Monitoring changes in the spot spacing is a result of the sample’s change in curvature and indicates an applied bending moment. Mounting techniques tested include using common cryogenic adhesives such as Apiezon N grease, GE varnish and Stycast epoxy as well as attaching samples in place on a copper cooling stage with copper wire and Teflon tape. Finally, the Cu sample stage is replaced with a Si sample stage in order to match the CTEs of the stage and the sample, leaving only the mismatch of a thin bonding layer. These techniques are compared and analyzed using a balanced force model and linear elastic/plastic theory to determine the degree to which each method stresses the sample.

Correlating Material Structure to Properties with High Spatial Resolution Using In situ and High Precision Electron Microscopy

Eva Olsson; Chalmers University of Technology, Gothenburg, Sweden.

In situ electron microscopy can be used to reveal the correlation between local atomic structure and properties. This talk will address in situ electron microscopy using local sample manipulation combined with the ability to measure the local electrical transport properties and effects induced by electric fields, light and mechanical strain. This is achieved by using a scanning tunnelling microscope in scanning electron microscopes and transmission electron microscopes [1-4] and by specially designed stages for uniaxial mechanical strain [5]. The electron microscopes provide both imaging capabilities and spectroscopy methods for the determination of local material and electronic structure. The use of scanning electron and transmission electron microscopes enables the in situ studies to be carried out on different length scales spanning from the subatomic dimension to micrometer. The position of individual atoms and atom columns can be determined with picometer precision [6]. The direct correlation on the small scale involving individual interfaces, defects and atoms provides access to new information about which microstructural constituents that are active in determining the material properties on the different length scales. It is possible to study both bulk and surface effects and understand how the properties can be tuned and the performance tailored for each specific application.

Influence of Cryogenic Mounting on Thermal Stress Measurements

Margaret H. Samuels1,2 and Christopher Richardson1; 1Laboratory for Physical Sciences, College Park, Maryland, United States; 2Materials Science, University of Rochester, Rochester, New York, United States.

Cooling samples to cryogenic temperatures is common for quantum materials and quantum information devices. Effective cooling requires adequate thermal conduction pathways between the cooling stage and the sample; however, many mounting techniques introduce materials with mismatched coefficient of thermal expansion. The mismatch may result in a bending moment or stress in the sample. Both can deform the sample while measurements occur, may cause plastic deformation, and potentially couple to the physical quantity of interest.

In this study, various mounting techniques are employed to create thermal conduction pathways between the cooling stage and the sample. A three-tiered structure of CTE mismatch (sample/mounting material/stage) is studied. Silicon wafers are good standard reference samples widely used across thin film research, are flat and mirror-like surfaces that will reflect a laser signal. The curvature of a Si wafer sample is measured in real time as a function of temperature. A projected pattern of laser spots is reflected from a piece of Si wafer that is mounted to a stage in a cryostat. Monitoring changes in the spot spacing is a result of the sample’s change in curvature and indicates an applied bending moment. Mounting techniques tested include using common cryogenic adhesives such as Apiezon N grease, GE varnish and Stycast epoxy as well as attaching samples in place on a copper cooling stage with copper wire and Teflon tape. Finally, the Cu sample stage is replaced with a Si sample stage in order to match the CTEs of the stage and the sample, leaving only the mismatch of a thin bonding layer. These techniques are compared and analyzed using a balanced force model and linear elastic/plastic theory to determine the degree to which each method stresses the sample.
grown on Si or Ge substrates; rather it must be grown on a relaxed Si$_{0.2}$Ge$_{0.8}$ virtual substrate. Demonstrations using RP-CVD have used a thick Ge layer grown directly on Si (001) that is combined with a reverse composition grading to Si$_{0.2}$Ge$_{0.8}$. These virtual substrates usually possess a rough surface and crosshatch morphology that needs chemical mechanical polishing before QW growth. This experimental study focuses on the growth and characterization of abrupt metamorphic Si$_{0.2}$Ge$_{0.8}$ buffer layers grown on Si (001) substrates by means of MBE. The Si and Ge fluxes are created with electron beam evaporation solid sources that are controlled by electron impact emission spectroscopy. In this proposed design, a fully relaxed Si$_{0.2}$Ge$_{0.8}$ layer is directly grown on Si (001) at a lower substrate temperature than what can be accomplished with RP-CVD. A strain balanced Ge/Si$_{0.2}$Ge$_{0.8}$ supper lattice is grown to filter threading dislocations followed by a relaxed Si$_{0.2}$Ge$_{0.8}$ spacer that also serves as the bottom barrier for the Ge QW. The 10 nm-thick Ge QW is grown with a Si$_{0.2}$Ge$_{0.8}$ top barrier layer and a 1-nm Si cap. Growth details and structural characterization of the materials using a variety of techniques will be described.

Quantum phenomena is at the heart of current condensed matter physics and materials science. Quantum oxide materials are one of promising candidates to study the quantum phenomena, owing to the strong coupling between various degrees of freedom. With more recent attention being paid to the topological state of matter, it is important to understand how this state influences different physical properties of oxides and how it is coupled to the conventional degrees of freedom in oxides.

In this tutorial we will cover various aspects of quantum behavior of oxides. The tutorial will focus on the transport properties and electronic structures of quantum oxide materials, and novel imaging techniques and theoretical approaches for characterization of the materials.

8:30 AM
Electrical and Thermal Transport Properties of Quantum Materials (From Basics to Dirac and Oxide Systems) Benoît Fauqué, ESPCI

In this tutorial I will give an introduction to the electrical and thermoelectric transport in solids. After an introduction on their experimental implementation I will show how these properties can be used to characterize the electronic ground states of the matter. I will particularly focus on the effect of a magnetic field on semi-metals which allows you to determine the Fermi surfaces (by the study of quantum oscillations) and can even generate new electronic state of the matter.

10:00 AM BREAK

10:30 AM
Electronic Structure of Quantum Oxides (Angle and Spin-Resolved Photoemission) Phil King; University of St Andrews

Angle-resolved photoemission spectroscopy (ARPES) is arguably one of the most direct momentum-resolved probes of the electronic structure of solids and their surfaces. The spectral function measured by ARPES encodes information on the many-body interactions of importance to determining a material’s properties, and, with recent developments in spin-resolved detection, can now additionally yield key insights on the momentum-resolved spin-polarisation of electronic states. As such, ARPES has proved a powerful probe of the quantum many-body states and phases of oxide quantum materials. In this tutorial, we will cover the basics of ARPES and its operation, and review some recent key results from surface and interface studies of oxide crystals and thin films.

SYMPOSIUM QN07

Emergent Phenomena in Oxide Quantum Materials
April 23 - April 25, 2019

Symposium Organizers
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characteristics for such applications. Mechanisms such as spin-polarized current injection, the spin Hall effect, and precessional spin pumping have been used to generate spin currents, while spin current may be detected by the inverse spin Hall effect or via spin transfer torque exerted upon a ferrimagnet.

We have recently demonstrated that X-ray detected ferromagnetic resonance (XFMR) provides unique capabilities to probe the generation and propagation of spin currents in multilayered spintronics structures directly [1]. Taking advantage of magnetic contrast and element specificity of X-ray magnetic circular dichroism (XMCD), we showed that in a Ni$_8$Fe$_{12}$/Cu$_{20}$/Mn$_{80}$/Cu$_{20}$/Co$_{20}$ multilayer, spin current excited in the Ni$_8$Fe$_{12}$ layer propagates across the Cu spacer layer and excites a precession in the Co layer.

In magnetic thin films, the amplitude of the magnetization precession is typically not isotropic, i.e. the magnetization vector does not precess on a symmetrical cone but rather on an elliptical trajectory with an amplitude of the precession varying along different directions perpendicular to the static applied field. The asymmetry reflects the magnetic anisotropy of the system. Making use of the fact that XMCD probes the magnetization component collinear with the direction of the incoming X-ray beam, we are able to measure the precession amplitude along orthogonal directions by choosing suitable experimental geometries. This allows us to determine the exact shape of the precession cone with element-selectivity, valence state specificity and sensitivity to the symmetry of the absorber site in complex oxides such as Ni$_{1-x}$Zn$_{1-x}$Al$_x$Fe$_2$O$_4$ (NZAFO) [2].

Moreover, utilizing the sensitivity of X-ray magnetic linear dichroism (XMLD) to antiferromagnetic order, allows for expanding the capabilities of X-ray detected magnetic resonance to antiferromagnetic systems. We will present our current efforts to probe the propagation of spin currents in ferrimagnetic materials as well as ferromagnetic/antiferromagnetic multilayer structures.

References

11:15 AM QN07.01.03

A Theoretical Outlook on the Properties of Spin Ice and Other Magnetic Pyrochlore Thin Films
Michel Gingras; Department of Physics and Astronomy, University of Waterloo, Waterloo, Ontario, Canada.

Frustrated magnetic materials and strongly correlated electron systems are a forefront of research in modern condensed matter physics and materials science. Despite almost three decades of investigations, the theoretical understanding of these fascinating systems remains incomplete. The most prominent theoretical frameworks used to tackle these systems take the form of an emergent gauge theory akin to the gauge theory that describes conventional electromagnetism.

Spin ice is an unusual substance in which the magnetic moments of individual atoms behave very similarly to the protons in conventional water ice — hence the name spin ice — failing to align even at very low temperatures and displaying the same residual entropy that Linus Pauling calculated for water ice and which is measured experimentally. Spin ices, which belong to the broad class of compounds called magnetic pyrochlores, actually have something in common in common with electromagnetic fields; both can be described by a gauge theory. Many aspects of conventional electromagnetism are sensitive to constraints from enclosure boundaries, such as total internal reflection used in communication with optical fibers. It is then reasonable to wonder if spin ices have similar sensitivities to boundary effects and confinement. Motivated by the recent experimental realizations of spin ice and other magnetic pyrochlore thin films, I will discuss in this talk some of the exotic physical phenomena that arise when considering spin ice thin films such as, for example, a novel magnetic charge crystallization on the film surface while the bulk remains thermally disordered [1]. From a broader context, magnetic pyrochlore thin films offer a natural platform to study the confinement of emergent gauge fields describing strongly correlated systems and the evolution of nontrivial magnetic correlations as one moves from three to two dimensional spin textures [2]. Finally, I will discuss the consequences of open surfaces on the mechanisms of order by disorder in thin films of the XY pyrochlore antiferromagnet. We find that a complex competition between multiple orders take place, as a function of temperature and film thickness. A gradient of ordering spreads over long length scale inside the film while the nature of the phase transitions is blurred between two and three dimensional critical phenomena [3].

Beyond the physics of films, this work also pertains to near-surface effects in single crystals of rare-earth pyrochlore oxides.


11:30 AM QN07.01.04

Interacting and Spin-Orbit Coupled Electronic States of Delafossite Oxide Natural Superlattices
Phil King; School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom.

The ABO$_2$ family of delafossite oxide metals can be considered as natural superlattice structures comprising high-conductivity metal layers separated by insulating transition-metal oxide building blocks. I will present our angle-resolved photoemission (ARPES) measurements from several members of this series. In PdCrO$_2$, the oxide layer is an antiferromagnetically-ordered Mott insulator, where we find that a coupling between the metallic and insulating subsystems renders photoemission sensitive to the spin susceptibility of the Mott layer [1]. In PdCoO$_2$ and PtCoO$_2$, the oxide layer is a band insulator, but this becomes hole-doped at the surface due to electronic reconstruction driven by a polar surface charge. We demonstrate how the resulting Co$_2$O$_4$ surface supports metallic states which host a surprisingly-large Rashba-like spin-orbit splitting, resulting from a structural configuration which ensures a large energy scale associated with inversion symmetry breaking at this surface [2]. For the Pd-terminated surface, we find how an electron self-doping, again driven by the surface polarity, mediates a Stoner transition to itinerant ferromagnetism [3], in contrast to the non-magnetic nearly-free-electron-like character of the Pd-derived states in the bulk [4]. Together, these results indicate the wide range of materials properties that can be stabilized in delafossites, as well as at their surfaces and interfaces.

Key collaborators on this work include Veronika Sunko (St Andrews and Max-Planck Institute for Chemical Physics of Solids, Dresden), Federico Mazzola (SIAM), Helge Rosner, Seunghyun Kim, Pallavi Kushwaha, and Andy Mackenzie (MPF-CFSS), Sota Kitamura and Takashi Oka (MPF-PKS), and Leonid Pourovskii and Antoine Georges (Collège de France).


SESSION QN07.02: Low-Dimensional Behavior
Session Chairs: Susanne Stemmer and Hua Zhou
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 127 C

1:30 PM QN07.02.01
Freestanding Crystalline Oxide Membranes and Heterostructures
Harold Hwang$^{1,2}$; $^1$Stanford University, Stanford, California, United States; $^2$SLAC National Accelerator Laboratory, Menlo Park, California, United States.

The ability to create and manipulate materials in two-dimensional (2D) form has repeatedly had transformative impact on science and technology. In parallel with the exfoliation and stacking of intrinsically layered crystals, the atomic-scale thin film growth of complex materials has enabled the creation of artificial 2D heterostructures with novel
functionality and emergent phenomena, as seen in perovskite oxides. We present a general method to create freestanding complex oxide membranes and heterostructures with millimeter-scale lateral dimensions and nanometer-scale thickness. This facilitates many new opportunities we are beginning to explore, including the topological melting transition of 2D crystalline order, the application of extreme strain states, and integration with other materials families.

2:00 PM QN07.02.02
Novel Epitaxial Strain Effects on the Hybrid Improper Ferroelectrics from First-Principles Xuezeng Lu and James Rondinelli; Northwestern University, Evanston, Illinois, United States.

Epitaxial strain is a powerful tool to generate ferroelectricity owing to polarization-strain coupling. Local lattice degrees-of-freedom such as rotations of metal-oxygen octahedral also couple to strain, and can be used to tune a material’s oxygen rotational-related properties such as metal-insulator transitions and magnetic reconstruction by strain. Here, we first use electronic structure calculations to investigate the strain effects on (001) thin films of the hybrid-improper ferroelectric (HIF) A$_2$B$_2$O$_2$ compounds. Surprisingly, other than the bulk polar Cmcm phase, we find a new nonpolar phase becomes the ground state under both experimentally accessible biaxial compressive and tensile strains, which is beyond the people’s believe about the role of the polarization-strain coupling. Furthermore, the generality of the polar-to-nonpolar (N-NP) transition in HIFs (not only in A$_2$B$_2$O$_2$ compounds) leads us to find a novel route to tune the physical properties that are classified as mechanical, optical and magnetic responses, which we also propose could be electric-field-tunable, near the P-NP phase transition boundary. Our results may offer a route to search for new functionalities in hybrid-improper ferroelectrics.

2:15 PM QN07.02.03
Realization of Room-Temperature Ferroelectric Ferromagnet via 1D Tetragonal Network Kyung Tae Kang, Chang Jae Roh, Jinyoung Lim, Taewon Min, Jun Han Lee, Kyoungjin Lee, Tae Yoon Lee, Seunghun Kang, Daehye Seol, Jiwooong Kim, Hojim Chi, Ahn Mihye, Seung Chul Chae, Yoon Seok Oh, Jaekwang Lee, Jaegun Yu, Jong Seok Lee and Woo Seok Choi; 1Sungkyunkwan University, Suwon-si, Korea (the Republic of); 2Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of); 3Seoul National University, Seoul, Korea (the Republic of); 4Pusan National University, Busan, Korea (the Republic of); 5Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 6Hokkaido University, Hokkaido, Korea (the Republic of).

Distortive modulation of the transition metal-oxygen (MoO$_3$) polyhedra provides an efficient strategy for designing the functional metal oxides. Ferroelectricity occurs as the collective distortion of the Mo$_6$ polyhedral network breaks a spatial inversion symmetry. For conventional perovskite oxides, ferroelectricity occurs owing to the ionic displacements within a 3D network of MoO$_6$ octahedra. Meanwhile, the polyhedral tilting and rotation within some 2D networks of Mo$_6$ (x = 5 or 6) polyhedra can also lead to centrosymmetry breaking through the trilinear coupling with the spontaneous polarization. This gives rise to the geometric ferroelectricity even in the oxides including magnetic ions, i.e., multiferroic.

Considering the fundamentally different principle of 2D network for ferroelectricity from that of 3D network, one can further suggest the 1D chain network to explore unprecedented nature of ferro-ordrings. Here we exhibit the combined partial distortion (CPD) induced ferroelectricity and coupled ferromagnetism in 1D chain network by investigating the brownmillerite SrFeO$_3$$_2$, epitaxial thin film of FeO$_2$ tetrahedra. The constrained distortion of low symmetry of FeO$_2$ tetrahedra leads to the simultaneous displacement of ions and rotation of the tetrahedra. The CPD further play a role in inducing cant ferromagnetism coupled with electric polarization via Dzialoshinskii-Moriya interaction. Our result provides a new paradigm for designing 1D MO$_6$ networks, expected to benific the emergent ferro-ordering materials including room-temperature ferroelectric ferromagnets.

2:30 PM QN07.02.04
Artificial 1D Quantum Stripes of Complex Oxides Ambrose Seo; Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky, United States.

Tuning the dimensionality of a system offers a useful tool for realizing new quantum phenomena associated with critical phase transitions and topological properties. However, only a few naturally occurring complex oxides with tunable, intrinsic 1D and 2D structures are available for experimental studies. In this talk, I will present a new approach of synthesizing 1D – 2D quantum stripe systems by creating dimensionally-confined superlattices from in-plane oriented layered materials. For example, we have demonstrated this method to synthesize 1D – 2D IrO$_2$ stripes using c-axis oriented superlattices of SrIrO$_3$ and insulating (La,Sr)IrO$_3$, both are of the K$_3$NiF$_4$ symmetry [1]. The dimensional confinement of the superlattices has been confirmed by structural characterizations. Optical spectroscopy shows clear anisotropic characteristics and dimensional electronic confinement of the spin-orbit coupled $J_{eff} = 1/2$ band. Spin and orbital excitations observed in resonant inelastic x-ray scattering spectra suggest larger exchange interactions and more confined orbital excitations in the 1D IrO$_2$ stripes as compared to its 2D counterpart. The observed electronic confinement and localized spin-structure are quite consistent with density functional theory calculations. This method of tuning the dimensionality between 1D and 2D via stripe-superlattices is a viable technique for obtaining dimensionality-induced quantum phase transitions, in which exotic excitations such as the fractional quantizations of quasi particles can emerge.


3:00 PM BREAK

SESSION QN07.03: Magnetic Properties of Oxide Quantum Materials
Session Chairs: Woo Seok Choi, Jaekwang Lee and Joo Bum Matsumo
Tuesday Afternoon, April 23, 2019
PCC North, 100 Level, Room 127 C

3:30 PM QN07.03.01
Strain-Induced Magnetic Transitions in Sr$_2$Mn$_5$O$_8$ Structure Yongjin Shin and James Rondinelli; Northwestern University, Evanston, Illinois, United States.

Sr$_2$Mn$_5$O$_8$ (SMO) in the C$_2$hMn$_5$O$_8$-type structure is one structure among A$_2$B$_2$O$_2$ compounds derived from ABO$_3$ perovskites with ordered oxygen vacancies (OOVs). The ordered arrangements of vacancies enable unique functional properties in such compounds, because the ligand-field modified orbital structure reconstructs as the octahedral BO$_6$ units are transformed into different BO$_5$, polyhedral arising from the OOVs. The magnetic order of transition metal oxides is governed by interaction of these orbitals and occupancy of electrons. For example, SMO exhibits a unique E-type antiferromagnetic (AFM-E) ordering because of the d$^4$ electronic configuration of Mn$^{3+}$ in the square pyramidal network. Hydrostatic pressure and biaxial strain provide additional routes to tune the magnetic properties of materials through lattice strain-induced changes to the orbital structure. Here, we investigate the relative stabilities of different magnetic orders realized through hydrostatic pressure and strain induced non-equilibrium local structures using density functional theory. We show that SMO hosts multiple magnetic transitions from AFM-C, AFM-E*, AFM-E, AFM-E*, and FM upon application of biaxial strain from compressive to tensile strain in (001) thin film geometries. In contrast, the AFM-E state is robust under hydrostatic pressure. As epitaxial strain produces anisotropic stresses, we observe different magnetic transitions depending on the relative orientation of the vacancy order with respect to the biaxial epitaxial strain. We conclude by summarizing the different changes in local structures and its impact on magnetic orders.

3:45 PM QN07.03.02
Engineering and Monitoring Spin Orientation in Anti-Ferromagnetic Oxide Multilayers Using X-Ray Spectroscopy Alpha T. N'Diaye, 1Mengmeng Yang, 2Qian Li, Elke Arendsholz, 1Zi Q. Qiu; 1Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2University of California, Berkeley, California, United States.

The majority of digital information is stored magnetically today. Nanoscale magnetic domains encode “1’s” and “0’s” on common commercial hard drives and newer magnetic data storage concepts rely on domain walls or parallel and antiparallel magnetization in magnetic multilayers. To develop novel materials and concepts for data storage applications, we
employ X-ray spectroscopy as well as X-ray magnetic dichroism to determine spin-states in a diverse range of materials. With the same tools, we are exploring new materials for data processing, as indications increase the the potential for further miniaturization of Silicon chips is soon to be exhausted.

The control of ferro- and antiferromagnetic spin orientation is a crucial element of today’s and tomorrow’s information technology applications, for instance needed for hard drive read heads or magnetic random access memory (MRAM). Novel device concepts using antiferromagnetic spintronics or antiferromagnetic skyrmions promise revolutionary innovations in information science. A detailed understanding of the mechanism which antiferromagnetic spin orientation is the prerequisite for pursuing these ideas.

With soft x-ray linear dichroism we follow the thickness dependent spin re-orientation in a NiO/CoO bilayer with varying CoO and NiO layer thicknesses. The oxide-oxide interface in this simple oxide system can be regarded as a model for the a supercell of complex oxide superlattices which have been used to demonstrate a host of new and exciting properties, such as interfacial ferromagnetism or novel electronic states.

In this simple system with negligible charge transfer or structural distortions we first investigate how the purely thickness dependent coupling between CoO and NiO forces the system from an antiferromagnetic in-plane spin orientation for larger CoO layer thickness to an out-of-plane spin orientation for thicker NiO. To this end we use a double wedge sample geometry which we locally probe with x-ray spectroscopy to access different thickness combinations ranging from 0-2.5nm for CoO and 0-14nm for NiO. We find the spin reorientation to be a consequence of the balance between interfacial coupling and bulk anisotropies of NiO and CoO.

Furthermore, we augment this system with a ferromagnetic Permalloy (Py) layer and show how an in-plane antiferromagnetic NiO spin configuration enhances the coercivity of the ferromagnetic permalloy layer substantially to ca. 400Oe while in the in-plane configuration the coercivity remains comparable to the coercivity of pristine Py.[1]


4:00 PM QN07.03.03
Spatially Resolving Spin Textures in Epitaxial Oxide Ferromagnet-Antiferromagnet Heterostructures Rajesh V. Chopdekar1, Yue Jiu1, Michael Lee2 and Yayoi Takamura2; 1Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Materials Science and Engineering, University of California, Davis, Davis, California, United States.

Recent interest in antiferromagnetic (AFM) spintronics has surged due to the possibility of obtaining ultrafast magnetization dynamics with no stray field, and complex oxide AFMs offer possibilities to engineer AFM spin textures via their many degrees of freedom and sensitivity to epitaxial strain. However, this lack of stray field makes imaging of the AFM domain structure difficult though conventional magnetic imaging techniques. This talk will discuss the use of x-ray photoemission electron microscopy (X-PEEM) with both x-ray linear and circular dichroism to spatially resolve the ferroic order in the AFM and ferromagnetic (FM) layers of a model system of alternating FM La0.7Sr0.3MnO3 and G-type AFM La0.7Sr2FeO4 (x=0 or 0.3). In the limit of few unit-cell thick layers for (001)-oriented samples, the AFM spin axis lies in the plane of the film in contrast to thicker layers where the spin axis cants out of plane. In contrast, (111)-oriented superlattices show markedly different behavior with two populations of spin orientations, a subset with spin axes canted along low-index <110> directions and which exhibit spin flop coupling to the FM layer, and a subset whose spin axis lies within the (111) plane. The coupling at the AFM/FM interface for both orientations allows for control of the AFM domain structure through magnetization rotation of the FM layer, and recent work has shown shape anisotropy offers an additional degree of freedom to control complex oxide AFM domain orientation. X-PEEM with variable temperature and x-ray polarization offers a powerful tool to determine the AFM spin axis on the scale of single AFM domains, and such a local probe is necessary for a full understanding of how the similar energy scales of shape anisotropy and interfacial exchange can be tailored in order to design spin textures in these oxide heterostructures.


4:15 PM QN07.03.04
Partial Magnetic Order in FePO4: Colin Sarkis1, Michael Tame1, James Neilson1, Hubro Cao2 and Kate Ross1; 1Colorado State University, Fort Collins, Colorado, United States; 2Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Competing antiferromagnetic interactions in triangular motifs of magnetic Fe3+ in the noncentrosymmetric compound FePO4 (spacegroup R3m) give rise to magnetic frustration. This leads to an unusual helical magnetic state below Ts=163K, in which needle-like domains exhibit long range antiferromagnetic order along the c axis, but have a correlation length restricted to ζ=7nm in the ab plane. Through single crystal neutron diffraction, we report a degenerate manifold of ordering wavevectors in the ab plane, which smear the incommensurate Bragg peaks into a continuous ring. We show this result to be consistent with the competition between J1 (nearest neighbor) and J2 (next nearest neighbor) interactions in a Heisenberg model, which produces a quasi-degenerate manifold of ordering wavevectors. When doped with non-magnetic Ga3+, polycrystalline samples show helical winding length and correlation length in the ab-plane to be equal. The restriction to short range order in the ab plane, along with the intimate connection of helical winding length and correlation length, imply the presence of a high density of non-trivial topological defects which are tied to the magnetic structure.

4:30 PM *QN07.03.05
Complex Magnetic Domain Structures in Oxides—Physical Origin and Device Application Jian Shen; Fudan University, Shanghai, China.

Physics of magnetic domains of conventional magnetic materials can be well described by minimization Landau-Lifshitz free energy. However, for magnetic oxides, competition between various types of exchange interactions has often led to complex magnetic domain structures that are far from being understood. One of the most typical example is the domain structure in colossal magnetoresistive manganites, which is featured by spatial coexistence of ferromagnetic, antiferromagnetic and even spin glass domains. These domains are not only different in magnetic states, but are also in different conducting states. By studying the effect of spatial ordering of the chemical dopants, we conclude that the dopants-induced disorder is the key reason for the formation of the complex domain structures in magnetic oxides. Based on the understanding of the physical origin of the complex magnetic domains in oxides, we have developed various methods to control the domain patterns in oxides and fabricated multi-bit memory device that can also carry out logic operations.
antireflection layer to greatly improve the absorption of near-infrared light, thereby overcoming the absorption limitation of near-infrared light. Instead of the conventional p-n junction and p-intrinsic-n junction, we introduce a ~15 nm thick alumina insulator layer introduced between a p-type Si substrate and n-type ZnO nanowire (NW) arrays, which are found that the charge carriers separation and collection efficiency have significantly enhanced. The photo-sensing responsivity and sensitivity are found to be nearly one order of magnitude higher than that of a reference device of p-Si/n-ZnO NW arrays, significantly higher than the commercial silicon photodiodes as well. The light-induced charge carriers flow across the appropriate thickness of insulator layer via the quantum mechanical Fowler-Nordheim tunneling mechanism. By virtue of the piezo-photoelectronic effect, the charge density at the interfaces can be tuned to alter the energy bands and the potential barrier distance for tunneling. Additionally, along with the use of incident light of different wavelengths, the influence of the insulator layer on the transport of electrons and holes separately is further investigated. The demonstrated concepts and study would lead to sensitivity improvement, quality enhancement of data transfer, decrease of power consumption and cost-reduction of silicon photonics.

**QN07.04.02**

**Performance Improvement REBCO Multilayers by Means of Surface/Interface Quantum Modulation**

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REBa2Cu3O7-x (REBCO, RE=rare earth) coated conductors (CCs) have the huge market potential for large scale of commercial applications due to their excellent superconducting properties. Up to now, the high cost is still a bottleneck for practical applications. The most effective way to reduce the cost is to increase critical current density $J_c$ of thick REBCO films. However, $J_c$ of REBCO films will decrease as the increasing of REBCO film thickness. In this work, we report the enhancement of $T_c$ and $J_c$ of REBCO films achieved through the surface/interface quantum modulation. REBCO multilayers were fabricated on CeO2/IBAD-MgO buffered metal tapes by pulsed laser deposition (PLD). At first, $Y_{1-x}Gd_xBa_2Cu_3O_y$ (YGBCO) films were grown on CeO2/IBAD-MgO buffered metal tapes. Then, metal nanoparticles such as Ag and In were grown on YGBCO films. Comparing with the pristine REBCO films, higher $T_c$ and $I_c$ were observed from the YGBCO films with metal nanoparticles. The $T_c$ and $I_c$ values were increased by 1K and 40A, respectively. Furthermore, the YGBCO/In doped CeO2 (CeO2:In) YGBCO hetero-structures were fabricated. It was found that the $I_c$ value of the YGBCO/ CeO2:In/YGBCO trilayers was almost doubled. Interaction at the interface comprises a variety of effects, such as epitaxial strain, interface defects, elemental inter-diffusion, interface charge layers, electrical charge transfer between layers, and others, which can improve the superconducting properties of REBCO films. The results provide the important insights into the superconducting property engineering of REBCO CCs by artificial microstructure control.

**QN07.04.03**

**YBa2Cu3O6+-δ Nano-SQUIDs Based on Tunnel Nano-Junctions Fabricated by Focused Helium Ion Beam Direct Writing**

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Focus helium ion beam (FHIB) materials modification is an emerging technique with the capability to make high-quality thin-film YBa2Cu3O6+-δ (YBCO) superconducting Josephson junctions [1]. In this method, ion irradiation converts the film from a superconductor to an insulator by disordering the crystalline lattice. No material is removed or etched, as a result nanoscale insulating features are obtainable for both Josephson junctions[2] and superconducting electrodes for devices such as superconducting quantum interference devices (SQUIDs) [3].

We investigate YBCO nano-SQUIDs to push the scaling limits. YBCO SQUIDs with loop dimension from 1.2 μm down to 10 nm have been fabricated. Current-voltage characteristics revealed high-quality of Josephson tunnel junctions with insulating barriers. Voltage modulation as a function of magnetic field was measured for the nano-SQUIDs by both an on-chip control line and external coil in a wide temperature range from 4.2 K up to ~50 K. The highest modulation voltage was ~0.8 mV for a single nano-SQUID, and the smallest magnetic flux effective area achievable was ~0.25 μm2. The flux noise characteristics was measured open loop using a small signal method, which showed a white noise of ~0.6 μΦ0/Hz1/2 for the Nano-SQUID with loop dimension 400 nm.

Acknowledgments: This work supported by AFOSR, NIH, NSF, and UCOP.

Reference


**QN07.04.04**

**Electronic Structure and Transport Properties in Bi2-xCaFeO3-y with Control of Oxygen Vacancy Content**

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Oxygen vacancies are ubiquitous in oxide systems, which can play important roles to cause interesting physical phenomena such as metal-insulator transition, magnetic and ferroelectric orders, and high-$T_c$ superconductivity. Oxygen vacancy concentration has been a key control parameter to modulate physical properties [1]. In this work, we study the electronic structure and transport properties of Ca-substituted BiFeO3 (BCFO) thin films with controlling the oxygen vacancy concentration [2]. BCFO films can spontaneously produce oxygen vacancies owing to the stable oxygen number of Fe3+ ions. The as-grown state can be transformed into an electrically-formed state through electro-migration of oxygen vacancies, thereby creating a spatially uniform stoichiometric hole doping region [3]. We measure conduction band and valence band spectra by using X-ray photoemission spectroscopy and find that a non-rigid polaronic band emerges in the hole doping system. In addition, we investigate temperature dependence of electronic transport leading to a disorder-driven formation of a Coulomb-gap state.


**QN07.04.05**

**Temperature Dependent Exchange Bias in EuO$_x$,Si**

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EuO$_x$ combines several interesting properties: large magneto-optical effects, colossal magneto-resistance, and enhanced Curie temperature due to bound magnetic polarons. EuO$_x$ is also one of a very few ferromagnetic insulators and, as an ultra thin film, very sensitive to interface effects. Utilizing pulsed laser deposition, we deposited a film of EuO$_x$, onto a Si substrate in order to create a ferromagnetic (FM)/anti-ferromagnetic (AFM)/Semiconducting (SC) interface,$\text{EuO}_x$/Si,$\text{EuSi}_3$/Si, for applications in spintronics (spin filters). X-ray diffraction indicates the film crystallize into a preferred EuO(111) orientation, it also indicates a clear presence of EuSi2 which suggests Si diffuses across MgO buffer layer into the EuO$_x$. Density functional theory calculations are employed to model the conduction and valence bands from Eu and O and compared to x-ray absorption spectroscopy data. A magnetic signature, revealed by x-ray magnetic circular dichroism measurements, suggests the presence of a magnetic order above the Curie temperature. Strong, temperature dependent exchange bias coupling, due to the AFM/FM interface of $\text{EuO}_x$/Si, is observed in magneto optical Kerr effect spectroscopy hysteresis loops. Additionally the temperature dependent oscillatory nature of the exchange bias suggests the AFM layer undergoes a magnetic moment flip. This study demonstrates the realization of a ferromagnetic/antiferromagnetic/semiconductor interface and will be beneficial to future spintronic applications.
Various forms of titanium dioxide (TiO₂) have been applied in several fields - including electronics, energy, as well as environmental engineering - all which capitalize on the semiconductor behavior of this inexpensive, abundant and chemically stable material. Both common crystal structures of TiO₂, rutile and anatase, have large band gap (3.0 and 3.2 eV, respectively) limiting the principal optical absorption to the short wavelength UV photons only. To further enhance the photocatalytic activity, and thus make TiO₂ suitable for solar applications, a number of strategies have been worked out in the last decade. While anatase is known to have much higher photocatalytic activity than that of rutile, their mixed-phases have been known to have superior activity and have been utilized as commercial catalyst for decades. The band alignment between anatase and rutile mixed phases plays the decisive role in carrier separation after photogeneration. Electrochemical impedance analysis has confirmed that the flat band potential of anatase is about 0.2 eV lower than that of rutile. At the interface of the two phases, the photoexcited electrons tend to transfer from the anatase to the rutile, which has been corroborated by many researchers. Therefore, engineering the junction between two phases is crucial to properly address photocatalytic behavior in anatase-rutile systems. In this study, two types of core-shell heterojunction TiO₂ NFs were synthesized by sequential hydrothermal, calcination, and impregnation processes. Rutile TiO₂ NFs core with anatase TiO₂ NFs shell is denoted as R@A TiO₂ NFs, and the reverse structure is denoted as A@R TiO₂ NFs. In our study, the photodegradation of organic dyes and Kelvin Probe Force Microscopy (KPFM) analysis were applied to shed light on the mechanism of the excited electron-hole pair separation. The results of photodegradation showed that the A@R TiO₂ NFs had the highest activity under UV-B and UV-A irradiation, being nearly 3-fold higher as compared to AEROXIDE® TiO₂ P25. The results in conjunction with KPFM measurements indicated that in the heterojunction structure, electron-hole pairs were efficiently separated and the excited electrons stayed in the anatase phase, and holes were injected to rutile phase. When the A@R TiO₂ NFs heterostructures are decorated with Pt nanoparticles, the nanocomposite is particularly active in photocatalytic hydrogen evolution from ethanol-water mixtures with a production rate of ~8,500 μmol/h·g. Our study not only explains the role of anatase-rutile junctions in photocarrier separation, but also projects the development of other efficient photocatalytic heterostructures for green energy production and conversion.

**QN07.04.07**

**New Types of Magnetic Two-Dimensional Electron Gases**

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Two-dimensional electron gases (2DEGs) at oxide interfaces provide unique playgrounds for the exploration for emergent phenomena which motivate not only new concepts but also applied research. The perovskite SrTiO₃ is composed of 3d electrons, and well established, oxygen vacancies and the magnetic proximity effect can be utilized to introduce magnetic moments (Δsp per T cantor) [1], generating well spin-polarized 2DEGs [2]. This offers us valuable opportunities to build up magnetic 2DEGs, which is centrally important for spintronics. While most of the previous works focused on the 2DEGs at LaAlO₃/SrTiO₃ interfaces, here we report on three new kinds of 2DEGs systems: anatase TiO₂-based 2DEGs induced by low-energy argon ion irradiation and the 2DEGs formed between a magnetic insulator EuO and a high-k perovskite KTaO₃.

**QN07.04.08**

**Relaxational Ferroelectricity of (111)-BaTiO₃ Epitaxial Films**

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BaTiO₃ (BTO) is an intensively studied ferroelectric material with several ground-state polar structures: tetragonal, orthorhombic and rhombohedral varying from room temperature to low temperatures.[1] BTO is known that tetragonal phase of which polarization is [001]-direction is the most stable at room temperature. BTO films were grown epitaxially on (111)-oriented SrTiO₃ substrates with an intermediate SrRuO₃ electrode by pulsed laser deposition in order to see the results of the competition between six stable polarization each at another room temperature. Here, we use spherical aberration-corrected scanning transmission electron microscope (STEM) to identify domain structures and phases. We demonstrate that the ferroelectric polarization domains of (111)-BTO at room temperature contain both tetragonal and orthorhombic phases, by measuring pm-scale atomic displacements of Ti-cations directly from the images. Furthermore, the domain sizes range down to a few nanometers. Such a peculiar domain configuration is in good agreement with our phase field simulation, which shows that the orthorhombic domain is bridging different 90° tetragonal domains as a way to relieve the elastic strain of domain walls. We believe that the phase coexistence along with miniaturized domains have given rise to relaxor-like behaviors in the (111)-BTO film as we observed. We have deposited SrTiO₃ thin-films on SrTiO₃ buffer layer, and the reverse structure is denoted as R@A TiO₂ NFs. In our study, the photodegradation of organic dyes and Kelvin Probe Force Microscopy (KPFM) analysis were applied to shed light on the mechanism of the excited electron-hole pair separation. The results of photodegradation showed that the A@R TiO₂ NFs had the highest activity under UV-B and UV-A irradiation, being nearly 3-fold higher as compared to AEROXIDE® TiO₂ P25. The results in conjunction with KPFM measurements indicated that in the heterojunction structure, electron-hole pairs were efficiently separated and the excited electrons stayed in the anatase phase, and holes were injected to rutile phase. When the A@R TiO₂ NFs heterostructures are decorated with Pt nanoparticles, the nanocomposite is particularly active in photocatalytic hydrogen evolution from ethanol-water mixtures with a production rate of ~8,500 μmol/h·g. Our study not only explains the role of anatase-rutile junctions in photocarrier separation, but also projects the development of other efficient photocatalytic heterostructures for green energy production and conversion. **Reference**


**QN07.04.09**

**Synthesis and Characterization of Freestanding SrIrO₃ Epitaxial Thin-Films**

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Mott insulating states formed in layered iridates, such as SrIrO₃, have recently attracted substantial interest due to their unexpected novel properties caused by the coexistence of strong spin-orbit interactions and electron correlations. Recent studies on SrIrO₃ have revealed the possibilities of novel phases such as potential high-Tc superconductivity with d-wave gap.1 However, even though much experimental work using different tuning parameters, such as lattice strain, pressure and chemical doping, has been done, superconductivity has yet to be observed in this material. Moreover, it is also puzzling that electron-doped SrIrO₃ bulk crystals are metallic while SrIrO₃ thin films with as much as 15% electron-doping are insulating.2 This discrepancy may be due to strain-induced defects which are common for thin-film systems.

We have deposited SrIrO₃ thin-films on SrTiO₃ substrates using SrAl₂O₃ buffer layer.4 The water soluble SrAl₂O₃ has been shown to generate strain-free thin-films.4 High quality samples were obtained by depositing SrIrO₃/SrAl₂O₃ heterostructures on SrTiO₃(100) substrates using pulsed laser deposition. X-Ray diffraction and reciprocal space mapping shows that the SrAl₂O₃ buffer layer is relaxed and the SrIrO₃ is partially relaxed with respect to the SrTiO₃ substrate. The optical transmission spectra show that the peak energies (both a and b) are blue shifted in the SrIrO₃/SrAl₂O₃ heterostructure as compared to the SrIrO₃ thin-film on SrTiO₃. Our results demonstrate that the structural and optical properties of SrIrO₃ thin-films can be tailored using SrAl₂O₃ buffer layers and we will further discuss the electronic properties of freestanding SrIrO₃ thin-films in comparison to SrIrO₃ single crystal and SrIrO₃ thin-films on different substrates.

Magnetoresistance of Semi-Metals and Lightly Doped Semi-Conductors

Although SrTiO$_3$ was the first oxide superconductor to be discovered, the nature of its superconducting state has been a longstanding subject of debate in the literature, reflecting in many ways the elusiveness of other families of superconductors, such as the cuprates. A striking feature is that superconductivity already appears at very low carrier densities, when the Fermi temperature is lower than the Debye temperature, which is at odds with BCS theory. Bulk, undoped SrTiO$_3$ is an incipient ferroelectric for which quantum fluctuations suppress a low-temperature transition to a ferroelectric ground state. Several recent proposals have suggested that there could be a connection between ferroelectricity and superconductivity of SrTiO$_3$. In this presentation, we will report on experiments that tune the superconducting states of SrTiO$_3$ thin films grown by molecular beam epitaxy. We will discuss the effects of proximity to ferroelectricity as well as other ground states on the superconducting transition temperature and critical fields.

Large unsaturated magnetoresistance has been recently reported in numerous semi-metals [1]. Many of them have a topologically non-trivial band dispersion, such as Weyl nodes or lines. In the first part of my presentation I will show that elemental antimony displays the largest high-field magnetoresistance among all known semi-metals. I will present a detailed study of the angle-dependent magnetoresistance and use a semi-classical framework involving an anisotropic mobility tensor to fit the data [2]. A slight deviation from perfect compensation and a modest variation with magnetic field of the components of the mobility tensor are required to attain perfect fits at arbitrary strength and orientation of magnetic field in the entire temperature window of study. In the second part I will discuss the case of lightly doped SrTiO$_3$–x [3]. At low temperature we find that SrTiO$_3$–x displays a large transverse ($j$⊥$B$) but also longitudinal ($j$//B) magnetoresistance which can be captured, like in the case of the semi-metals, by a semi-classical framework including a field dependent mobility carriers.

Our results demonstrate that large orbital magnetoresistance is an unavoidable consequence of low carrier concentration and the sub-quadratic magnetoresistance seen in many semi-metals and doped semi-conductors can be attributed to field-dependent mobility, expected whenever the disorder length-scale exceeds the Fermi wavelength [4].

3. C. Collignon and al., unpublished

Quantum Phenomena in Interfacial 3d-5d Oxide Heterostructures

The non-trivial spin topology protects the spin texture against disorder and fluctuations, leading to substantial potential to miniaturize, store, and transport information with excellent stability and efficiency. Significant efforts have been focused on harnessing the Dzyaloshinskii-Moriya (DM) interaction, which results from strong spin-orbit coupling combined with broken inversion symmetry to generate magnetization rotations with fixed chirality and is a highly effective mechanism to generate skyrmions. To date, the most promising results have been achieved in multi-layer systems, which benefit from cooperative DM interactions from multiple interfaces and possible additional stabilization from inter-layer magnetic coupling of skyrmion columns. Furthermore, recent studies have identified the important roles of interfacial oxygen, hybridization, and charge transfer in determining the sign and strength of DM interactions. Transition metal oxides, in particular those containing heavy 5d elements, also possess the requisite materials parameters necessary for skyrmion formation. However, the majority of the studies focused on non-oxide-based systems. In this talk, we will present our observations on charge transfer induced magnetism, anomalous Hall effect, topological Hall effect in interface engineered 3d-5d transition metal oxide heterostructures. The critical role of the DMI and its interfacial control will be discussed together with the potential of 5d transition metal oxides for developing novel quantum materials.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

Ferromagnetic Order Above 1000 K in a Double Perovskite Osmate Synthesized by Molecular Beam Epitaxy

In the magnetic insulating oxides, it is known that the cubic crystal symmetry is favorable for higher Curie temperatures ($T_C$) [1], since the network morphology hosting the mechanisms of exchange interactions is subject to the crystal symmetry. So far, these oxides are typically 3d transition metal oxides where spin-orbit coupling (SOC) is tiny. An enhancement of the SOC in 5d systems is a promising way to boost the long range ferri/ferromagnetic (FM) order. For example, it was shown for a pyrochlore osmate (Ca$_2$OsO$_6$) that the SOC is responsible for its long range order [2]. Here we show that a highly B-site ordered cubic double-perovskite Sr$_3$OsO$_6$, which satisfies above criteria, surpasses the
long standing $T_c$; (943 K for spinel ferrite $\text{LiFeO}_3$) [3] record in all insulators and oxides by more than 100 K. We synthesized the magnetic insulator Sr$\text{OsO}_6$, by molecular beam epitaxy (MBE) on (001) SrTiO$_3$ substrates (300-nm thick). Atomic-resolution scanning transmission electron microscopy (STEM) along with diffraction (TED) measurements have revealed the cubic structure and excellent Sr/Os ordering on the B'/B-site. For double perovskites, it is well known that the crystal symmetry is dominating the exchange interactions, e.g., SrFeMoO$_6$ ($T_c = 415$ K, cubic) [4] and SrFeWO$_6$ (antiferromagnetic, $T_N = 37$ K, monoclinic) [5]. Thus, the finding new property of Sr$\text{OsO}_6$ plays a crucial role for the emergence of high $T_c$, which is an electronically isostructural compound, Ca$_2$Os$_6$, having a monoclinic structure, exhibits $T_c = 50$ K. Owing to optical band gap of ~2.65 eV in Sr$\text{OsO}_6$, the electronic charge carriers move by hopping between localized electronic states, and this is supported by the temperature dependence of resistivity ($\rho$); $\rho(T) \propto T^{1+\delta}$ (variable range hopping model), along with the high resistivity value ($\rho(300 \text{ K}) = 75 \text{ 2cm}$).

Using density functional theory calculations based on a Pariser-Parr-Pople (PPP) functional, we reproduced the ferromagnetic ground state of Sr$\text{OsO}_6$. We show that the large SO of the Os$^{5d}$ orbitals indeed drive the system toward an insulating state with $J_{\text{eff}} = 3/2$ [6]. Our calculations reveal that the $J_{\text{eff}}$ states are split into effective total angular momenta of $J_{\text{eff}} = 3/2$ (doublet) and $J_{\text{eff}} = 1/2$ (singlet) states. The $J_{\text{eff}} = 3/2$ states are fully occupied with two 5$d$ electrons per Os$^{5d}$, resulting in an insulating state. Our experimental results for Sr$\text{OsO}_6$ show that in $5d$ systems extraordinary high $T_c$ is possible in spite of the long distance (5.81 Å) between 5$d$ ions. The $J_{\text{eff}} = 3/2$ insulating state with $T_c$ above 1000 K is thus consequences of the cubic rock-salt type environment of Os$^{5d}$ ions and the enhanced SOC found in Sr$\text{OsO}_6$. Further investigations, e.g., XMCD, are required to analyze the hitherto unidentified exchange interactions.


11:15 AM QN07.06.03

**Discovery of a New Quantum Dimer Magnet on a Strongly Spin-Orbit Coupled Honeycomb Lattice—Yb$\text{Si}_2\text{O}_5$**

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A significantly strong Bose-Einstein condensate (BEC) of magnetic ions would be a milestone in the field of quantum magnets.

In this presentation we will report the observation of a giant inverse Edelstein effect in NiFe/LaAlO$3$/SrTiO$3$ heterostructures, with spin-to-charge conversion one order of magnitude more efficient than in previous systems [8]. Moreover the large dielectric constant of the STO substrate makes possible the use of a back-gate voltage $V_g$ to modulate the Rashba effect. This can be interpreted in terms of a crossover between the occupancy of one to several bands with different orbital characters and different spin–orbit textures. Our recent experiments suggest that oxide interfaces have a strong potential for spintronics, both for the generation or detection of spin currents through direct or inverse Edelstein effects, and for spin-based quantum computing. Spin currents, which are at the heart of spintronics, allows the electrical control of magnetic (and resistance) states in magnetic nanostructures. In this context, there is a huge interest in finding new techniques for the efficient generation and manipulation of spin currents, especially using the spin-orbit interactions in non-magnetic materials. This has been greatly facilitated by the discovery of the Rashba effect, a manifestation of spin-orbit interaction (SOI) in solids, where the spin degeneracy associated with the spatial inversion symmetry is lifted due to a symmetry-breaking electric field normal to the heterointerface [5].

The Rashba effect is a manifestation of spin-orbit interaction (SOI) in solids, where the spin degeneracy associated with the spatial inversion symmetry is lifted due to a symmetry-breaking electric field normal to the heterointerface [5].

Edelstein has realized that in a Rashba two-dimensional electron system, the flow of a charge current is accompanied by a non-zero spin accumulation [6] coming from uncompensated spin textured Fermi surfaces. The reverse effect, corresponding to a spin-to-charge conversion through SOI (inverse Edelstein effect), was first demonstrated at Ag/Bi(111) interfaces [7].

In this presentation we will report the observation of a giant inverse Edelstein effect in NiFe/LaAlO$3$/SrTiO$3$ heterostructures, with spin-to-charge conversion one order of magnitude more efficient than in previous systems [8]. Moreover the large dielectric constant of the STO substrate makes possible the use of a back-gate voltage $V_g$ to modulate the 2DES carrier density and electronic properties. By this way, we found that the amplitude of the converted current can be modulated over one order of magnitude, and even changes sign. This can be interpreted in terms of a crossover between the occupancy of one to several bands with different orbital characters and different spin–orbit textures. Our recent experiments suggest that oxide interfaces have a strong potential for spintronics, both for the generation or detection of spin currents through direct or inverse Edelstein effects, and for their electrical modulation. Moreover, our observation of a very large spin-to-charge conversion efficiency at an interface with a moderate Rashba splitting highlights the importance of a long scattering time, and for the design of novel Rashba enhancement of electrical insulation from metallic layers are carefully engineered. We will compare the conversion efficiency of STO/LAO interface with that of the Spin Hall effect of metals, other Rashba interfaces and surface of Topological Insulators. We will also show that this record value can even be much enhanced by tuning carefully the heterostructure.

First-Principles Study of the Origin of N-Type 2DEG in LaAlO$_3$/SrTiO$_3$ (111) Heterostructure

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The emergent discovery of two-dimensional electron gas (2DEG) in LaAlO$_3$/SrTiO$_3$ (LAO/STO) heterostructure has attracted considerable attention over the past decade. Recently, unlike strongly localized 2DEG in LAO/STO (001) heterostructure, a wide n-type 2DEG density distribution is reported in the LAO/STO (111) interface (K. Song et al., Nat. Nanotechnol. 13, 198 (2018)). According to the polar catastrophe scenario, the LAO/STO (111) interface consisting of [Ti]$^+2$ and [LaO$_3$]$^-$ layers is expected to exhibit the highly localized p-type characteristics. Despite these controversies, the origin of n-type 2DEG at the LAO/STO (111) interface has not been clearly revealed yet. Here, we carry out first-principles density functional theory calculations to reveal the origin of n-type 2DEG widely distributed through the the interface of LAO/STO (111) heterostructure. We find that the n-type 2DEG originates from extra electrons created by the oxygen vacancy at the [[LaO$_3$]$^-$] terminated LAO (111) surface, and these excess oxygen vacancies significantly modulate the relative displacements between La and oxygen atoms and octahedral rotations in LAO layers. The presence of oxygen vacancy, atomic displacement modulation and octahedral rotation in the vicinity of LAO (111) surface are confirmed by annular dark-field scanning transmission electron microscope image at the atomic scale.

Anomalous Exchange Bias Induced by Hidden Interface in Oxide Heterostructures

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Advances in thin film synthesis enable unique opportunities to enhance and control the physical properties of interfaces by controlling the interactions in complex oxides. It is well known that interface layers provide opportunities to create or control functional properties of oxide heterostructures. However, the role of such an interfacial layer in controlling functionalities has not been fully explored. In this talk, the influence of buried interfaces in oxide heterostructures on their magnetic properties will be discussed. A shift of the magnetization hysteresis along the applied field axis was observed. We show the loop shift is an exchange bias (as opposed to the shift of a minor loop) and is present in single phase manganite thin films. Interestingly, the sign of exchange bias is controlled by the cooling field strength. When the cooling field is small, negative exchange bias is observed while positive exchange bias was observed for cooling fields exceeding a threshold. The origin of such an exchange coupling is related to the pinned interfacial layer, confirmed by polarized neutron reflectometry. Our results shed new light on using oxide interfaces to design functional devices.

Interface functionality in oxide heterostructures can be controlled by strain engineering, due to the nearly degenerate ground states of competing order in these systems. A central question is which role structural reconstructions can be used to establish and control new magnetic spin textures. In general probing antiferromagnetic spin structures are difficult, and we present data on the interplay between AF spin axis of LFO and the occurrence of magnetic reconstructions at the (111)-oriented LSMO/LFO interface. To probe the spin texture of the different layers, we rely on a combination of soft x-ray spectroscopy, x-ray photoemission electron microscopy and polarized neutron reflectometry. Our results shed new light on using oxide interfaces to design functional devices.
non-trivial electronic states. Recently, both AMR and AHE have also attracted significant attention in antiferromagnetic metals and semiconductors. For example, significant AHEs in non-collinear antiferromagnets have been discovered. Another phenomenon of recent interest is the potential coupling between the orientation of the Niel vector and the topology of the electronic states in antiferromagnets with symmetry-protected Dirac and/or Weyl. Both AHE and AMR can serve as signatures of such interactions. While an elegant theoretical framework exists for the intrinsic AHE and its connection to the Berry curvature of the electronic bands, AMR remains comparatively less well understood. The degenerately doped antiferromagnetic semiconductor EuTiO$_3$ is a unique testbed for these ideas for several reasons. Despite a small net magnetization, it exhibits an intrinsic AHE that changes sign as a function of the carrier density. We report on the symmetry of the anisotropic magnetoresistance (AMR) in doped EuTiO$_3$ films as a function of the applied magnetic field. Multiple transitions in the AMR symmetry are observed and are attributed to magnetic field induced changes in the band topology. In particular, at high fields a transition from positive to negative magnetoresistance is observed, which coincides with change from four-fold to two-fold symmetry in the AMR. This indicates a non-trivial phase transition in the electronic structure. We discuss the results in the context of Weyl points that form in the band structure of the EuTiO$_3$ as a function of magnetic fields.

4:15 PM *QN07.08.03 Quantum Transport in Magnetic Semiconductor EuTiO$_3$ Films Kei Takahashi$^{1,2}$, Kazuki Maruhashi$^3$, Tomoki Murata$^1$, Qing Y. Wang$^1$, Hiroaki Ishizuka$^1$, Mohammad S. Bahramy$^{1,1}$, Sunao Shimizu$^1$, Ryosuke Kurihara$^1$, Atsushi Miyake$^1$, Masashi Tokunaga$^1$, Naoto Nagaosa$^{4,1}$, Yoshinori Tokura$^{2,5}$ and Masashi Kawasaki$^{1,2}$. RIKEN, Wako, Japan; PRESTO, Japan Science and Technology Agency (JST), Tokyo, Japan; 3Institute of Physics, Chinese Academy of Sciences, Beijing, China; 4Institute for Solid State Physics, University of Tokyo, Kashiwa, Japan; 5Department of Applied Physics and Quantum Phase Electronics Center, The University of Tokyo, Tokyo, Japan.

Quantum properties in oxides have been well explored in correlated electron systems with rich interplay among charge-spin-orbital degrees of freedom in electrons, now extending the playground to a variety of topics such as spin-orbit, Weyl, and edge states. Research on quantum transport in high electron mobility oxides started from such conventional semiconductors as ZnO and SrTiO$_3$(STO). To extend the research further, EuTiO$_3$(ETO) is an ideal system by adding a knob of magnetic control (local 4$f^7$ moment on Eu$^{3+}$). We employ a metalorganic gas source molecular beam epitaxy (MOMBE) at very high substrate temperature that enabled us to observe quantum Hall effect in STO quantum well [1]. The mobility in ETO films has reached to 300 and 3,000 cm$^2$/Vs at 2 K, respectively, for strained and strain-free states. Those films show unique quantum properties due to crystal-field and Zeeman splittings, respectively.

In the case of strained films, we observed additional terms in the anomalous Hall effect during the magnetization process, which is not proportional to the magnetization, caused by the type II Weyl nodes in the conduction band [2]. For the strain-free films, Shubnikov–de Haas (SdH) oscillations turned out to be clearly observable at the ferromagnetic state. Our band calculation suggests that the oscillating bands, originally derived from Ti 3d orbitals, are fully spin polarized and modified by the f-d coupling between Eu 4f and Ti 3d orbitals. These new findings strongly suggest that the electron-doped ETO film with high mobility is an ideal magnetic semiconductor to explore novel magneto ‘quantum’ transport phenomena.


SESSION QN07.09: Ionic Movement in Oxide Quantum Materials
Session Chairs: Julia Mundy and Chan-Ho Yang
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 127 C

9:00 AM *QN07.09.01 Electric Field Control of Magnetism Through Proton Evolution Pu Yu. Tsinghua University, Beijing, China.

Ionic substitution during the growth forms an essential pathway to manipulate the carrier density, leading to a rich spectrum of electronic states in strongly correlated systems. To obtain a further control of the functional materials after the growth, the electrostatic charge modulation methods through dielectrics, ferroelectrics and ionic liquids have been widely employed, demonstrating great reversible tunability. However, an intrinsic limitation of these electrostatic approaches is that they are only effective for materials with thicknesses of a few nanometers, due to the short screening length of the charge carriers. Recently the electric-field induced ionic evolution demonstrates a great tunability of bulk compounds. Among the studies, the hydrogen ion (proton) attracts particular attention due to its comparatively small radius as well as easy accessibility. In this talk, we will demonstrate an efficient and reversible control of the carrier density in a series of strongly correlated oxide systems through the ionic liquid gating induced protonation. The insertion of protons electron-dopes the materials, leading to an exotic magnetic phase transition along with the increase of proton concentration. We envision that electric-field controlled protonation opens a new avenue systematically control the electric and magnetic field phase diagram in strongly correlated complex oxide systems.

9:30 AM QN07.09.02 Reversible Control of Oxygen Vacancy Ordering in 2D and 3D Lattices Using Active Strain and Voltage Pulses Lide Yao, Sampo J. Inkinen and Sebastiaan van Dijken; Aalto University, Espoo, Finland.

Oxygen defects can have a profound effect on the physical properties of transition metal oxides. In complex oxides where magnetic, ferroelectric and superconducting phases emerge from strong correlations between localized transition metal electrons, oxygen vacancies can radically alter a plurality of quantum phenomena via valance changes and structural phase transitions. The ability to control the concentration and profile of oxygen vacancies in oxide nanostructures would thus open up comprehensive prospects for new functional ionic devices.

Here, we use in situ transmission electron microscopy (TEM) to demonstrate reversible switching between uniform structural phases in epitaxial La$_2$Sr$_{1.5}$MnO$_5$ films. In our experiments, we employ a piezo-controlled probing holder to apply short voltage pulses and local strain. Simultaneous high-resolution imaging and resistance probing under zero strain reveals reproducible voltage-induced order transitions in a low-resistance perovskite phase, a high-resistance La$_2$Sr$_{1.5}$MnO$_5$ brownmillerite structure, and an intermediate-resistance perovskite-like phase [1]. Reversible horizontal migration of oxygen vacancies within the manganite film, driven by combined effects of Joule heating and bias voltage, predominantly triggers the structural and resistive phase transitions. Concurrent application of perpendicular strain and voltage pulses produces an entirely new structural phase whereby oxygen vacancies order in regular 3D rather than 2D patterns.


9:45 AM QN07.09.03 Tuning Electron Correlation in Low-Dimensional Vanadium Oxides—Implications for Multivalent-Ion Cathode Materials and Next-Generation Computing Materials Justin L. Andrews, Abhishek Parij and Sarbajit Banerjee; Texas A&M University, College Station, Texas, United States.

Charge ordering and the localization of electrons in periodic wells is an intrinsic property of extended solids. Synthetic approaches that allow for precise control over the property are greatly desirable; however, systematically modulating periodic electron localization with some measure of tunability of the electron migration barriers represents a difficult challenge. The wider energy dispersion of bands when directly compared to discrete molecular orbitals in single molecules typically favors far greater delocalization of electrons and the multiplicity of sites implies that dimensional confinement of carriers can be established only for low-dimensional crystallographic motifs. One promising approach to modifying carrier density is by varying the electronic coupling across adjacent metal sites, but such attempts often result in phase transitions to entirely different crystal structures. Given the complexity of the problem, the chosen chemical system should exhibit electronic behavior spanning extremes between highly correlated and itinerant. Vanadium oxides represent such a system due to availability of multiple accessible redox states and an unequalled variety of structural motifs that can accommodate the intercalation of ions spanning the breadth of periodic table to create a diverse set of ‘bronzes’ with the stoichiometry M$_x$V$_y$O$_z$. Finally, vanadium has narrow V 3d-bands and the resulting oxides tend to crystallize in low dimensional motifs which surprisingly have the ability to avoid collapse upon topochemical transformations. Successfully achieving precise control over the
strength of electron correlation in this system has significant implications for the design of materials in disparate fields. Two such examples include the design of multivalent ion cathode materials and the design of materials that exhibit controllable and reversible electronic instabilities.

As a first example, charge localization in battery cathode materials represents a significant obstacle. In fact, coupling of a highly localized electron to a phonon mode hinders diffusion of the donated electrons through the vanadium oxide framework and must be addressed through chemical modification of the cathode material. Although moving beyond Li\textsuperscript{+} to Mg\textsuperscript{2+} and other divergent species presents the holy grail of sustainable battery technology, charge localization for the doubly-polarizing divalent ions becomes a significant problem, with only a small number of materials capable of this difficult feat. An alternative approach to mitigate the self-trapping of polarons is to utilize metastable phase space to design vanadium oxide frameworks that mitigate charge localization in $\alpha$-V$_2$O$_3$. We have recently shown that metastable phases ($\gamma$-V$_2$O$_3$ and $\gamma'\text{-}V_2$O$_3$) introduce frustrated coordination environments which facilitate cation diffusion and mitigate charge localization, enabling the reversible intercalation of Mg\textsuperscript{2+} and Ca\textsuperscript{2+}, respectively.

As a second example, one solution to the breakdown in Dennard scaling between transistor size and power density is to replace the traditional metal-oxide-semiconductor field-effect transistors (MOSFET) with novel computing architectures that exploit complex two-dimensional superconducting systems. Highly correlated materials which exhibit superconductivity at the precursors of an electronic transition are of interest because they can switch internal resistance values (often from metallic to insulating) rapidly upon external perturbation of the system; however, tailoring the temperature or gate-voltage threshold of these electronic transitions is critical. Modulation of this threshold and its magnitude requires precise control over charge localization and electron diffusion barrier to promote electronic transitions. We have recently reported examples of method for tuning electron correlation in M$_x$V$_2$O$_5$ bronzes with electronic instabilities through dimension reduction, interlayer separation, and stoichiometry.

10:00 AM BREAK

SESSION QN07.10: Exotic Superconductivity
Session Chairs: Manuel Bibes, Hiroshi Kohno and Jobu Matsuno
Thursday Morning, April 25, 2019
PCC North, 100 Level, Room 127 C

10:30 AM *QN07.10.01
Demystifying the Growth of Superconducting Sr$_2$RuO$_4$ Thin Films
Hari P. Nair; Cornell University, Ithaca, New York, United States.

Sr$_2$RuO$_4$ is an unconventional superconductor with potentially a spin-triplet, odd-parity superconducting ground state. There are many reports of high purity single crystals of Sr$_2$RuO$_4$ with $T_c$ up to 1.5 K. Furthermore, recent studies on Sr$_2$RuO$_4$ single crystals have shown that the $T_c$ can be further increased up to 3.5 K using uniaxial strain. To date, however, there are only three published reports of superconducting Sr$_2$RuO$_4$ thin films and the $T_c$s achieved are significantly below 1.5 K. This relative paucity of superconducting thin films is likely due to the extreme sensitivity of the odd-parity superconducting ground state in Sr$_2$RuO$_4$ to disorder. According to recent theoretical predictions, biaxially strained epitaxial thin films with isotropic in-plane strain can potentially maintain the topologically nontrivial $p_x \pm i p_y$ superconducting ground state while simultaneously enhancing $T_c$ by tuning the Fermi level towards a van Hove singularity. Thin films also provide a pathway for scalability, which is critical for potential practical applications of spin-triplet superconductors such as qubits for ground-state quantum computing. Here, we outline and demonstrate a thermodynamic growth window to achieve repeatable growth of superconducting Sr$_2$RuO$_4$ with higher $T_c$ than all prior thin films using molecular-beam epitaxy. We will also present some preliminary evidence of epitaxial strain-induced tuning of $T_c$.  

11:00 AM QN07.10.02
Metal-Insulator Transition in High Transition Temperature Superconductor Josephson Junction Barriers
Ethan Cho, Hao Li, Yan Ting Wang and Shane Cybart; University of California, Riverside, Riverside, California, United States.

We will present a study of Josephson junctions created with direct-write focused helium ion irradiation. Josephson devices were created by irradiating a narrow channel across a superconducting electrode with a focused helium ion beam. We studied how the irradiation dose affected the electrical transport properties such as critical current and voltage state resistance. For lower doses of irradiation, the critical current rapidly increased with decreasing temperature consistent with a metallic barrier junction. Whereas for higher doses the critical current approaches a maximum value like that seen in conventional insulating barrier Josephson junctions. Furthermore, we observed a continuous transition from metallic to an insulating behavior in the voltage state resistance with increasing dose. This transition can be modeled with a single parameter related to barrier strength which is directly proportional to the irradiation dose.

11:15 AM QN07.10.03
Synthesis and Electronic Configuration of Infinite-Layer Nickelate Thin Films
Danfeng Li\textsuperscript{1,2}, Matthias Hepping\textsuperscript{1,2}, Haiyu Lu\textsuperscript{3}, Xiao Feng\textsuperscript{3}, Yasuyuki Hikita\textsuperscript{4}, Chunjing Jia\textsuperscript{1,2}, Brian Moritz\textsuperscript{2}, Eugenio Paris\textsuperscript{5}, Yi Tieng\textsuperscript{1}, Zahid Hussain\textsuperscript{6}, Yi-De Chuang\textsuperscript{6}, Zhi-Xun Shen\textsuperscript{1,2}, Thorsten Schmitt\textsuperscript{1}, Thomas P. Devereaux\textsuperscript{1,2}, Wei-Sheng Lee\textsuperscript{6} and Harold Wang\textsuperscript{1,2}; Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California, United States; Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California, United States; Paul Scherrer Institut, Villigen, Switzerland; Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; SSRL, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

In the quest for analogs to high-$T_c$ cuprates, nickelates stand out as a promising candidate and have received considerable research interest, due to their electronic structure potentially being in proximity to that of the cuprates. The strategy is therefore to engineer the electronic structure of nickelates to resemble the key ingredients of cuprates, such as a half-filled single band near the Fermi level, antiferromagnetic correlations in the undoped parent compound (S\textsuperscript{=})\textsuperscript{1/2}, and hybridization between $d_{x^2-y^2}$ and $e_g$ orbitals and oxygen ligands. Here, we present the synthesis of an infinite-layer nickelate (LaNiO$_2$) thin film, where the Ni ions have square planar coordination with O in quasi-2D NiO$_2$ planes [1], using a low temperature metal hydride reduction process [2]. We study its electronic structure, in comparison with that of an isostructural cuprate (SrCuO$_2$) thin film, by using x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) at the O K- and Ni L-edges.


11:30 AM QN07.10.04
Coexistence and Competition Between Ferromagnetism, Rashba Spin-Orbit Coupling and Superconductivity in Oxide 2DES
Daniele Storza\textsuperscript{1,2}, Benoit Jourault\textsuperscript{1,2}, Emiliano Di Gennaro\textsuperscript{1,2}, Roberto Di Capua\textsuperscript{1,2}, Alessia Sambri\textsuperscript{1,2}, Davide Massarotti\textsuperscript{1,2}, Maria D'Astuauno\textsuperscript{1}, Fabio Miletto Granozio\textsuperscript{1}, Francesco Tatone\textsuperscript{1,2} and Marco Salluzzo\textsuperscript{1}; University of Naples Federico II, Napoli, Italy; SPIN, CNR, Naples, Italy; Laboratoire Charles Coulomb, UMR 5221, CNRS, Université Montpellier 2, F-34095, Montpellier, France.

Two dimensional electron systems (2DES) formed at the interface between insulating transition metal oxides have demonstrated an extraordinary range of properties. The coexistence among these properties can be studied via electric field effect, making oxide 2DES an ideal test bench for the investigation of novel quantum phenomena. A notable example is the coexistence between superconductivity and Rashba spin-orbit coupling in the 2DES at the interface between LaAlO$_3$ and SrTiO$_3$ (LATO/STO). We will review the recent remarkable progress in understanding complex LAO/STO superconducting nanodevices [1], which can shed some light on the nature of superconductivity in LAO/STO, and focus on indications of the presence of an unconventional superconducting order parameter obtained in LAO/STO based Josephson junctions [2]. The large and electric field tunable Rashba spin-orbit coupling shown by the LAO/STO 2DES is also of interest for possible spintronic applications [3]. A viable route for electric field control of the spin transport in spintronic devices requires, however, the creation of a spin polarized current. We will present the transport properties of a spin polarized oxide 2DES realized using a thin layer of delta doping EuTiO$_3$ (ETO) intercalated between LAO and STO [4] and demonstrate how ferromagnetism and Rashba spin-orbit coupling in this heterostructure can be controlled via electric field effect and temperature [5].
Berry Phase Engineering at Oxide Interfaces  
Andrea Cavigliala  
Kavli Institute of Nanoscience, TU Delft, Delft, Netherlands.

Geometric phases in condensed matter play a central role in topological transport phenomena such as the quantum, spin and anomalous Hall effect (AHE). In contrast to the quantum Hall effect—which is characterized by a topological invariant and robust against perturbations—the AHE depends on the Berry curvature of occupied bands at the Fermi level and is therefore highly sensitive to subtle changes in the band structure. A unique platform for its manipulation is provided by transition metal oxide heterostructures, where engineering of emergent electrodynamics becomes possible at atomically sharp interfaces. We demonstrate that the Berry curvature and its corresponding vector potential can be manipulated by interface engineering of the correlated itinerant ferromagnet SrRuO3 (SRO). Measurements of the AHE reveal the presence of two interface-tunable spin-polarized conduction channels. Using theoretical calculations, we show that the tunability of the AHE at SRO interfaces arises from the competition between two topologically non-trivial bands. Our results demonstrate how reconstructions at oxide interfaces can be used to control emergent electrodynamics on a nanometer-scale, opening new routes towards spintronics and topological electronics.

2:15 PM  QN07.11.02  
Exotic Magnetic Interlayer Coupling in Atomically Designed SrRuO3/SrTiO3 Superlattices  
Seung Gyo Jeong1, Sungmin Woo1, Jiwon Kim1, Youngmin Kim1,2, Sungkyun Park1, Hu Young Jeong1 and Woo Seok Choi1; 1Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of); 2Center for Integrated Nanostructure Physics, Institute for Basic Science, Suwon, Korea (the Republic of); 3Department of Physics, Pusan National University, Pusan, Korea (the Republic of); 4UNIST Central Research Facilities and School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Magnetic properties of perovskite SrRuO3 (SRO, a ferromagnetic metal) epitaxial thin films are strongly affected by the Ru-O bonding geometry, electronic structure, and dimensionality. Therefore, atomically precise oxide superlattices composed of SRO and SrTiO3 (STO, a nonmagnetic insulator) is an attractive model system to modulate and study the complex magnetic interaction. Various magnetic phenomena such as interlayer exchange coupling, quantum confinement, and spin-lattice coupling near the oxide interfaces can be investigated. In this presentation, we precisely and systematically control the number of atomic unit cell layers of SRO and STO in atomically designed SRO/STO superlattices. By controlling both the thicknesses of SRO and STO layers using pulsed laser epitaxy, we first demonstrate the structure-dependent magnetization of the artificial crystal. A strong correlation between the lattice symmetry (or Ru-O bonding geometry) and ferromagnetic ordering could be realized. In addition, we observed exotic magnetic interlayer exchange coupling between the ferromagnetic SRO layers across the insulating STO layer. Possible mechanisms for the unprecedented magnetic ground state behavior are suggested and discussed.

2:30 PM  QN07.11.03  
Margaret Mc Cartner1, Sujit Das2, Yun-Lang Tang3, Christoph Klewe2, Padraic Shafer4, Elke Arenholz2, Javier Junquera1, Lane W. Martin2 and Ramamoorthy Ramesh1; 1Department of Physics, University of California, Berkeley, Berkeley, California, United States; 2Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; 3Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 5Departmento de Ciencias de la Tierra y Fisica de la Materia Condensada, Universidad de Cantabria, Cantabria, Spain.

Emergent topologies in ferroelectric heterostructures—the polar analogs of magnetic vortices and skyrmions—have become a recent topic of interest for their potential to host exotic functionalities (e.g., emergent chirality and negative capacitance). These topologies can be stabilized in low-dimensional ferroelectrics. Superlattices of PbTiO3/SrTiO3 have proven to be particularly fruitful in this area; for example, the existence of polar vortex structures in such superlattices grown on DyScO3 substrates has been demonstrated. Furthermore, polar skyrmion structures have been observed in PbTiO3/SrTiO3 superlattices grown on SrTiO3 substrates using a combination of scanning transmission electron microscopy, X-ray diffraction, and second-principles calculations. Using resonant soft X-ray diffraction, we study the chirality of these polar skyrmions and show that the skyrmions have a preferred handedness. The origin of the circular dichroism is shown to be a chiral configuration of the titanium orbitals in the skyrmions.
Understanding and manipulating oxygen octahedral rotations have been subjects of much recent interest, and particular octahedral rotations are now parameters used in the design of new perovskite materials and heterostructures. As examples, modifications to the Ni-O-Ni bond angle in the nickelates have a profound effect on the temperature of metal–insulator transition, and changes to the octahedral rotation angles in the manganeseates promote different types of antiferromagnetic order. Although ferroelectricity is not conventionally related to oxygen octahedra, it has been predicted that geometrically modulated octahedral rotations can induce ferroelectric behavior, which is promising for the design of cross-coupled multiferroics. Control over the oxygen octahedral framework is widely recognized as key to the design of functional properties in perovskite oxide heterostructures. Although the oxygen octahedral framework can be manipulated during synthesis, the as-grown oxygen octahedra generally remain fixed, preventing the development of adaptive behavior in electronic and ionotonic systems. Theoretical calculations have shown that the coupling between oxygen octahedra and an external electric field is typically very weak if present at all, due to the geometrical centricity of octahedra. Therefore, it is considered extremely challenging to dynamically tune octahedral rotation by electric field.

In this talk, we will demonstrate that oxygen octahedral rotations can be dynamically and reversibly manipulated by an electric field when in the presence of defects, leading to significant changes in the electronic properties of a perovskite oxide during linear lattice distortion. Employing in situ synchrotron X-ray techniques to investigate heterostructures of the simple perovskite WO$_3$, we find that while application of a negative voltage leads to only subtle changes in structure and electronic properties, positive voltages have a dramatic effect on the oxygen octahedral rotation due to defect injection. The process is fully reversible, with the material returning to its original state after the gate voltage is removed. The results of density functional theory show that some octahedral rotation angles depend more strongly on the oxygen vacancy concentration than others and that both rotations and defects alter the electronic structure. Ionic liquid gating not only allows switchable defect structure and behavior by an electric field, but also provides a means of attaining the dynamic manipulation of octahedral rotations and the associated correlated properties. Such tunable properties can be used to establish nonequilibrium rotation patterns not available by static methods and facilitate the development of low-power electronics. Our results illustrate a highly effective approach for dynamically tuning the oxygen octahedral rotation in perovskite heterostructures for applications in oxide electronics and ionotronics.

3:45 PM QN07.12.03

Atomic Dynamics in VO$_2$: Across the Metal-Insulator Transition—Ultrafast Transition and Equilibrium Thermodynamics Olivier Delaire, Simon Wall, Shan Yang, Luciana Vidas, Matthieu Chollet, Michael Glownia, Michael Koziwa, Tetsuo Katayama, Thomas Henighan, Mason Jiang, Timothy Miller, David Reis, Lynn Boatner, and Mariano Trigo; 1Duke University, Durham, North Carolina, United States; 2ICFO–The Institute of Photonic Sciences, Barcelona, Spain; 3SLAC National Accelerator Laboratory, Menlo Park, California, United States; 4Japan Synchrotron Radiation Research Institute, Sayo-Gun, Japan; 5Stanford University, Palo Alto, California, United States; 6Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Vanadium dioxide (VO$_2$) can be switched from an insulating to a metallic state with either ultrafast laser pulses [1] or heating above $T_{MT}$=340K [2,3]. In both the photoexcited and thermal transitions, the insulator-to-metal transition (IMT) is accompanied by a structural change from a monoclinic (M1) to a rutile (R) structure, and numerous prior efforts have focused on elucidating the evolution of both the electronic and lattice degrees of freedom. The photoexcited transition occurs in a time scale of hundred femtoseconds, and while ultrafast X-ray diffraction has provided tremendous insight into the atomic dynamics during such ultrafast transformations, diffraction peaks alone probe only an average over multiple unit cells and are less sensitive to deviations from the average atomic path connecting the initial and final state. To overcome this limitation, we use femtosecond total x-ray scattering (diffuse and Bragg) from the LCLS x-ray free-electron laser to study the dynamics of the structural transition of bulk VO$_2$ at all length-scales [1]. We observe that the structural transition proceeds by uncorrelated disordering of the vanadium ions from their initial dimerized distribution [1], rather than the previously proposed synchronized motion along an optical phonon mode. After photoexcitation, the system explores a large volume of the available phase-space in a timescale comparable with a single phonon oscillation [1,2]. Our ab-initio molecular dynamics simulation quantitatively match our ultrafast x-ray scattering measurements, and show an unusual highly anharmonic, flat potential energy surface for the quasi-rutile structure in the photoexcited state, developing on femtosecond timescales and disrupting the vanadium dimers of the M1 phase by populating a continuum of modes. The rapid evolution after photoexcitation is enabled by the large phase space of phonon modes with low-frequency $\nu$-vibrations, which was also noted in [2] to yield a large phonon entropy gain stabilizing the rutile phase, and the strong damping of phonons in the rutile phase. Our current observations thus reveal an interesting parallel between the ultrafast and the thermal transitions. These results overture our current understanding of an archetypical ultrafast phase transition and provide new microscopic insights into rapid evolution toward equilibrium in photoexcited matter.


4:00 PM QN07.12.04

Ultrafast Control of Material Properties Through Non-linear Lattice Dynamics from First Principles Guru Khalsa and Nicole A. Benedek; Cornell University, Ithaca, New York, United States.

The development of intense ultrashort mid and far infrared laser sources has created an opportunity for functional materials based on the direct excitation of infrared active phonons. Strong excitation of infrared active phonons can produce sizable unidirectional distortions of crystal structure through non-linear coupling to other phonons. Complex oxide ceramics provide an important test-ground for this experimental approach due to their diversity, strong coupling to optical fields, and demonstrated connection between subtle structural changes and functional properties.

Our recent theoretical efforts in perovskite oxides explore selective control of functional properties that exploit nonlinear lattice dynamics induced by the excitation of infrared phonons. Using first-principles techniques we predict that ultrafast optical control of magnetism is experimentally accessible in rare-earth titanates and show that, when combined with strain, this optical technique exposes a magnetic phase inaccessible in the equilibrium phase diagram.

4:15 PM QN07.12.05

Field Induced Phases of the XY Pyrochlore Er$_3$Sn$_2$O$_7$: Danielle Yahnle, Ludovic Jaubert, Michel Gingras, Darren Pereira, Duminda Sanjeewa, Joseph Kolis and Kate Ross; 1Colorado State University, Fort Collins, Colorado, United States; 2University of Bordeaux, Bordeaux, France; 3University of Waterloo, Waterloo, Ontario, Canada; 4Clemson University, Clemson, South Carolina, United States; 5Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Er$_3$Sn$_2$O$_7$ has been proposed as an example of the dipolar XY antiferromagnetic (AFM) pyrochlore. This system is theorized to undergo a first order phase transition to an ordered phase known as the Palmer-Chalker (PC) phase. The behavior of Er$_3$Sn$_2$O$_7$ has been found to be somewhat enigmatic, however, with neutron scattering measurements revealing the emergence of the PC state at a lower temperature than predicted, via an apparently second order transition. In addition, slow dynamics have been observed throughout the low temperature regime, including within the PC state. These deviations from theoretical expectations have been attributed to quantum fluctuations resulting from a competition between classical ordered eigenstates. We report on field dependent specific heat measurements on Er$_3$Sn$_2$O$_7$. In zero field, we find a slightly higher phase transition temperature than previously reported. In finite field, we find a reentrant phase diagram that compares well quantitatively with classical Monte Carlo simulations only in the high field region of the phase diagram. This provides further evidence of strong quantum fluctuations in Er$_3$Sn$_2$O$_7$ in low fields, suggesting its proximity to a quantum disordered regime.
Colloidal Nanoparticles—From Synthesis to Applications
April 22 - April 26, 2019

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SESSION QN08.01: Nanoparticle Synthesis and Applications I
Session Chairs: Mei Cai and Hongyou Fan
Monday Morning, April 22, 2019
PCC North, 100 Level, Room 129 B

8:30 AM *QN08.01.01
Growth and Transformation of Colloidal Nanostructures in Confined Spaces Yadong Yin; University of California, Riverside, Riverside, California, United States.

Colloidal nanostructures have been studied quite extensively in the research area of heterogeneous catalysis long before the introduction of the concept of nanoscience and nanotechnology. The significant progress achieved in the past twenty years in chemical synthesis has enabled precise control over not only the size but also the shape of the metal nanostructures, and therefore attracted intense interest not only in catalysis but also optoelectronics due to the well-known effect of localized surface plasmon resonance. In this presentation, I will introduce our recent progress in the synthesis of colloidal metal nanostructures in confined spaces using various templating methods, their chemical transformation behavior, and further manipulation of their secondary structures. By combining the confinement of templates with the seed-mediated growth strategy, we demonstrate the significant advantages of this general method over the conventional ones in creating a large variety of nanomaterials with novel plasmonic properties.

9:00 AM *QN08.01.02
On the Prenucleation Stage of Colloidal Semiconductor Quantum Dots Kui Yu; Sichuan University, Chengdu, China.

A worldwide interest during the past thirty years has been witnessed in the development of colloidal semiconductor nanocrystals (NCs). With significant efforts on the control of the size and size distribution, NC synthesis has been performed as an empirical art, lacking of fundamental understanding of the pre-nucleation stage also called the induction period. Colloidal semiconductor quantum dots (QDs) and magic sized clusters (MSCs) have been observed to evolve in a reaction together, sometimes. In this presentation, I will present our systematic study on their formation pathways. Based on our experimental data, we propose that there are two individual pathways in the prenucleation stage of the formation of QDs. The LaMer model of the classical nucleation theory (CNT) describes one pathway and the self-assembly of the cation and anion precursors is the other pathway which results in the formation of MSCs. We believe that our exploration of the prenucleation stage moves one step forward towards mechanism-enabled design and synthesis of NCs.

9:30 AM *QN08.01.03
Ultrafast Photophysics Dynamics In Situ Quantum Dot Devices Jianbo Gao; Clemson University, Clemson, South Carolina, United States.

Quantum dot devices have wide applications in photovoltaics, optoelectronics, and sensors due to quantum dot unique quantum confinement effect, which can be tailored by size, shape, structure, and composition. Therefore, the ultrafast photophysics dynamics of charge carrier in situ devices (electrons, holes, or ions) including carrier transport, injection through optical or electrical, recombination, trapping, and transfer is one of the most fundamental questions.

We developed ultrafast photocurrent spectroscopy and ultrafast electroluminescence spectroscopy to address the ultrafast carrier dynamics in situ devices including solar cells, single-photon detectors, light emitting diodes, and photodetectors. In addition to that we understand ultrafast carrier transport and recombination dynamics, we discover novel photoconductivity phenomena, which cannot be addressed by other laser pump-probe spectroscopies.

10:00 AM BREAK

10:30 AM *QN08.01.04
Whole Cell Pathogen and Small Molecule Analytical Detection with Aptamer-Functionalized Particles Susana Diaz-Amaya1, Li-Kai Lin1, Amanda Deering2 and Lin Shang1; 1School of Materials Engineering, Neil Armstrong Hall of Engineering, Purdue University, West Lafayette, Indiana, United States; 2Department of Food Science, Philip E. Nelson Hall of Food Science, Purdue University, West Lafayette, Indiana, United States.

Infectious outbreaks caused by foodborne pathogens such as E. coli O157:H7 are still occurring worldwide and cause acute illnesses and significant industrial impact. As a chemical component of organic materials, bisphenol A (BPA) is used in the food and consumer products industries. Despite its benefits, low-dose exposure to BPA adversely affects human health because it is an endocrine disrupting chemical (EDC). We present on the feasibility of using aptameric DNA sequences, covalently conjugated to colloidal nanoparticles, for the sensitive and highly specific detection of whole cell pathogens and small molecule toxic molecules via surface enhanced Raman spectroscopy (SERS) analysis. Low concentrations of E. coli O157:H7 were detected (~10^4 CFU/mL) and quantified (~10^3 CFU/mL) within 20 minutes in both pure culture and ground beef samples. We also report on a new range-extended bisphenol A (BPA) detection method that includes high-SERS-performance gold nanoparticles, i.e., 40 nm gold nanostars (GNSs) and 4-aminothiophenol (4-ATP) as Raman reporters. The limit of detection for BPA was 0.073 ppb, which is 205 and 20 times more sensitive than those of visual intensity and color intensity quantifications, respectively.

11:00 AM QN08.01.05
Stoichiometric Preparations of Iron Oleate to Improve the Reproducibility of Iron Oxide Nanoparticle Syntheses Dale L. Huber1, Sergei A. Ivanov2, Erika Vreeland1 and John Watt1; 1Sandia National Laboratories, Albuquerque, New Mexico, United States; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3IR Dynamics, Albuquerque, New Mexico, United States.
Iron Oleate has long been one of the most popular precursors for the synthesis of high-quality iron oxide nanoparticles. This is true despite the fact that it is not commercially available and must be custom synthesized. There are a handful of related syntheses that are in common use, but reproducibility of the synthesis is a significant concern. Iron oleate does not readily form a simple complex with one iron atom bonded to three oleate ligands as one might imagine. Instead, iron oleate often exists as a complex mixture of species that includes a series of oligomeric species with iron atoms bonded to each other through oxo bridges as well as other structure. This non-stoichiometric mixture is not easily purified as iron oleate resists the most common purification approaches. Iron oleate can not be recrystallized, as it does not crystallize and instead forms an oil or glass depending upon its temperature. Washing approaches are difficult to reproduce as the oleate ligands can be very labile, and repeated washes will continue to remove oleate ligands until it finally forms an insoluble solid. This lack of control also makes it difficult to purify the compound through chromatography as the compound can decompose on the column. Unfortunately, differences in the precursor synthesis can lead to difficulty in reproducing nanoparticle syntheses. We will discuss two approaches that have been demonstrated to yield highly reproducible iron oleate precursors. In the first approach, we produce iron oleate through the decomposition of another organometallic species in an excess of oleic acid yielding a solution of known stoichiometry that can be used without purification. In the second approach, judicious selection of reagents, solvents, and reaction conditions can yield an isolated compound of pure iron oleate with an iron:oleate ratio of exactly 1:3. These compounds can then be used to enhance the reproducibility of iron oxide nanoparticle syntheses. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the DOE’s National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States government.

11:15 AM QN08.01.06 Structural Transformations of Functional Nanoparticles Zewei Quan; Chemistry, Southern University of Science and Technology, Shenzhen, China.

Novel materials with new properties are often realized by modifying their structures of existing materials without altering their composition. One of the approaches is to apply a high pressure to a material. In this part, I will show how to take advantage of another scaling law - nanoparticles as single structural domains to investigate PbTe nanoparticles by high-pressure method. Reversal of Hall-Petch effect concerning the structural stability to particle size was first reported on PbTe nanoparticles. Based on this novel observation, the pressure-dependent amorphizations on 5 nm PbTe nanoparticles was further utilized to harvest the metastable amorphous PbTe nanoparticles of great technological applications. Then, I will also talk about how to use pressure to engineer the bandgap of photovoltaic perovskites. Finally, the phase engineering of metastable Au nanostructures is also delicately achieved and the atomic transition path is revealed.

11:30 AM QN08.01.07 High ON-Current Vertical Field-Effect Transistors Based on Environmentally-Benign Quantum Dots Jeongkyun Roh, Hyeong Jin Yun and Victor Klimov; Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Colloidal quantum dots (QDs) have gained considerable attention as a new class of nanomaterials that can potentially enable the next-generation solution-processible electronic and optoelectronic devices (Science 353, 85523, 2016). Owing to their superior optical properties, intense studies on QD-based color converters, light-emitting diodes (Nature 515, 96, 2014, Nat. Photon. 12, 159, 2018) and solar cells (Nat. Nanotechnol. 13, 456, 2018) have been underway leading to successful commercialization of the QD-display technology. The next frontier is exploration of electronically coupled QD solids in the context of prospective applications in solution-processible flexible electronics toward wearable electronic and sensing systems. One existing challenge in this area is low mobility of non-toxic QDs, which limits performance characteristics of non-toxic QD-based field-effect transistors (FETs) that represent basic building blocks of electronic circuits. Low mobilities lead to low ON-currents of typical QD-FETs. Increase in the current is possible by reducing the FET channel length, however, this would require the use of expensive and non-scalable patterning methods such as e-beam lithography. Here, we demonstrate high ON-current QD FETs based on environmentally-benign QDs by employing a vertical architecture, which is a vertical stack of a gate electrode, a gate insulator, a source electrode, semiconductor transport layer, and a drain electrode. Using this approach, we reduce a channel length down to sub-nanometer scale, and as a result, achieve an unprecedented ON-current of ~0.1 A/cm² in p-type QD FETs, which is three orders of magnitude higher than in standard lateral FETs. This notably high ON-current of vertical QD FETs is demonstrated using non-toxic Zn-doped CuInSe₂; QDs (J. Am. Chem. Soc. 138, 4201, 2016) and achieved despite their low hole mobility of ~0.001 cm²/Vs. A switchable behavior of a vertical FET is enabled by the porous structure of a source electrode, which allows for the gate-controlled electric field to penetrate into a vertical channel and modulate a charge carrier density. The pattern of the source electrode is defined by optical interferometric lithography, which is a simple, fast, scalable and mask-less patterning method. To improve switching properties of the FET, a charge-blocking layer was applied to the top surface of the patterned source electrodes. This allows us to steer the charge flow in a lateral direction along the gate oxide interface, which is the channel region well-modulated by gate bias. Furthermore, we demonstrate polarity control of QD vertical FETs by employing a simple complex with one iron atom bonded to three oleate ligands as one might imagine. Instead, iron oleate often exists as a complex mixture of species that includes a series of oligomeric species with iron atoms bonded to each other through oxo bridges as well as other structure. This non-stoichiometric mixture is not easily purified as iron oleate resists the most common purification approaches. Iron oleate can not be recrystallized, as it does not crystallize and instead forms an oil or glass depending upon its temperature. Washing approaches are difficult to reproduce as the oleate ligands can be very labile, and repeated washes will continue to remove oleate ligands until it finally forms an insoluble solid. This lack of control also makes it difficult to purify the compound through chromatography as the compound can decompose on the column. Unfortunately, differences in the precursor synthesis can lead to difficulty in reproducing nanoparticle syntheses. We will discuss two approaches that have been demonstrated to yield highly reproducible iron oleate precursors. In the first approach, we produce iron oleate through the decomposition of another organometallic species in an excess of oleic acid yielding a solution of known stoichiometry that can be used without purification. In the second approach, judicious selection of reagents, solvents, and reaction conditions can yield an isolated compound of pure iron oleate with an iron:oleate ratio of exactly 1:3. These compounds can then be used to enhance the reproducibility of iron oxide nanoparticle syntheses. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the DOE’s National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States government.

11:45 AM QN08.01.08 The Importance of ‘Beneficial Impurities’ in Surfactant Assisted Synthesis of Colloidal Nanoparticles Yuval Golan; Department of Materials Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel.

While surfactant assisted synthesis is probably the most common technique for the preparation of colloidal nanoparticles, workers in the field often encounter severe irreproducibility issues. In this talk, we will present several examples, from our work [1,2], as well as by others [3-5], for the role of ‘beneficial impurities’ in nanoparticle synthesis. Furthermore, a new binary phase of cubic nanocrystalline semiconductors has been discovered in recent years in the form of colloidal nanoparticles. The first materials to be discovered were π tin mono-sulfide [6,7] and π tin mono-selenide [8], yet density functional theory calculations predict the existence of additional potentially useful compound semiconductors in the π structure. [9] There is growing experimental evidence that phase control in the tin mono-chalcogenide system is likely to be governed by ‘beneficial impurities’ as well.

References


SESSION QN08.02: Nanoparticle, Synthesis, Assembly and Applications I

1:30 PM QN08.02.01
Fabrication of Arrays of Highly Complex Noble Metal Nanostructures Using Nanoimprint Lithography in Combination with Liquid-Phase Epitaxy

Svetlana Neretina, Robert Hughes, Spencer Golze, Arin Preston and Trevor Demille; University of Notre Dame, Notre Dame, Indiana, United States.

Current best-practice lithographic techniques are unable to meet the functional requirements needed to enable on-chip plasmonic devices capable of fully exploiting nanostructure properties reliant on a tailored nanostucture size, composition, architecture, crystallinity, and placement. As a consequence, numerous nanofabrication methods have emerged that address various weaknesses, but none have, as of yet, demonstrated a large-area processing route capable of defining organized surfaces of nanostructures with the architectural diversity and complexity that is routinely displayed in colloidal syntheses. Here, a hybrid fabrication strategy is demonstrated in which nanoimprint lithography is combined with templated dewetting and liquid-phase syntheses that is able to realize periodic arrays of complex noble metal nanostructures over square centimeter areas. The process is inexpensive, can be carried out on a benchtop, and requires modest levels of instrumentation. Demonstrated are three fabrication schemes yielding arrays of core–shell, core–void–shell, and core–void–nanoframe structures using liquid-phase syntheses involving heteroepitaxial deposition, galvanic replacement, and dealloying. With the field of nanotechnology being increasingly reliant on the engineering of desirable physicochemical responses through architectural control, the fabrication strategy provides a platform for advancing devices reliant on addressable arrays or the collective response from an ensemble of identical nanostructures.

2:00 PM *QN08.02.02 Si Microparticle Based Electrode for Effective Stress Relaxation and Stable Electrochemical Cycling Donghyuk Kim1, Minkyu Park1, Hyunghchoul Shin2, Seungmin Hyun3 and Seung Min Han1; 1Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Si anode of a lithium ion battery undergoes extreme volume expansions during lithiation and delithiation cycles. Finite element analysis indicates that significant build-up of lithiation-induced stresses can develop that results in fracture of the Si anode material. In this study, we report two different designs for Si microparticle based composite anode that allows for relaxation of the diffusion induced stresses in the Si microparticles. Self-healing polymer and Si microparticle freestanding composites was proposed and analyzed for its cyclic stability that confirmed enhanced retention, with the freestanding composite demonstrating 91.8% capacity retention after 100 cycles at C/10 rate. Second design for the composite anode uses Si microparticles that are embedded in combustion reacted, nanoporous ZnO. The nanoporous ZnO was shown to in itself undergo conversion reaction that hence increased the capacity and was able to help the coalescence of SiMPs for enhanced electrochemical cycling, which yielded a binder-less design with an initial capacity of ~3,900 mAh/g at C/20 rate and a reversible capacity of ~1,500 mAh/g beyond 200 cycles at C/5 rate. In addition, the Li2O/ZnO matrix derived from conversion-reacted nanoporous ZnO acted as an effective buffer to lithiation-induced stresses from volume expansion and served as a binder-like matrix that contributed to the overall electrode capacity and stability.

2:30 PM *QN08.02.03 Hybrid Metal–Inorganic Nanoparticle—Core–Shell Dendrimers and Star Copolymers Rigoberto C. Advincula1; Case Western Reserve University, Cleveland, Ohio, United States.

The preparation of new nanomaterials requires hierarchical levels of ordering and structuring: from molecular to macroscopic. Much has been demonstrated in metal, metal oxide, inorganic nanoparticles by way of size, shape, and polydispersity control. The Plasmonic and emissive properties dependent on size, shape, and hot spots are well known. Dendrimers and other hyperbranched polymer systems are of interest for their functionality in catalysis, drug delivery, reactivity, etc. Of high interest are dendrimer functionality in electro-optical applications and nanomedicine. This includes dendrimers capable of hierarchical ordered and self-assembly. We highlight the convergence synthesis of a variety of hybrid nanoparticle dendrimers and their electropolymerizability. The synthesis of precise dendrons as modular building blocks for functional dendrimers and the use of star copolymers for various core-shell architectures are demonstrated. Our group has reported a number of these hybrid systems and have reported the step-by-step routes towards structure-property relationships. These has resulted in controlled charge -transfer and energy transfer properties not to mention the ability to provide greater stability for these nanoparticles. What is also important is the use of surface sensitive spectroscopic and microscopic analytical tools applied rationally to highlight evidence of order and function.

3:00 PM BREAK

3:30 PM *QN08.02.04 Design Nanostructured Si materials for Practical Anodes of Next Generation Li-Ion Batteries Xiaolin Li, Haiping Jia and Ji-Guang Zhang; Pacific Northwest National Laboratory, Richland, Washington, United States.

Nanostructured materials have been found to be critical in promoting the performance of energy storage and conversion devices, such as batteries. Here, several nanostructured Si materials have been designed for practical anodes of high energy Li-ion batteries (LIBs). In one effort, the large (~20 μm) mesoporous Si sponge have controlled porosity and pore size, which can limit the particle volume expansion at full lithiation to ~30% and prevent pulverization of bulk particles. The porous Si anodes deliver a specific capacity of up to ~750 mAh/g based on the total electrode weight and >80% capacity retention over 1,000 cycles. The electrodes with the loading of ~1.5 mAh/cm2 demonstrated ~92% capacity retention over 300 cycles. The composite electrodes of porous Si and graphite (~3 mAh/cm2 loading) with a specific capacity of ~650 mAh/g demonstrate ~82% capacity retention over 450 cycles. In another effort, hierarchical structured Si/CNT microspheres developed not only have good porous structure to accommodate the volume expansion and achieve ~30% apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to ~200 MPa pressure. The anodes deliver a high specific capacity of ~1500 mAh/g and 85% capacity retention over 200 cycles at the areal loading of ~3 mAh/cm2.

4:00 PM QN08.02.05 Light Activated Synthesis of Periodic Arrays of Metallic Nanoplates Robert Hughes, Svetlana Neretina, Spencer Golze and Sergei Rouvimov; University of Notre Dame, Notre Dame, Indiana, United States.

Our laboratory has developed a new synthetic procedure for generating periodic arrays of metallic nanostructures shaped as hexagonal or triangular nanoplates using a room temperature light-activated growth mode. Such structures have the potential to act as interactive components for the detection of biological and chemical analytes using various sensing modalities (e.g., Surface Enhanced Raman Scattering (SERS)). The synthesis is reliant on the formation of Au seeds exhibiting planar defects – without such defects the growth mode is deactivated. Through the engineering of defects, which have been extensively studied using Titan TEM imaging and electron diffraction, such structures have now and achieve ~30% apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to ~200 MPa pressure. The anodes with the loading of ~1.5 mAh/cm2 demonstrated ~92% capacity retention over 1,000 cycles. The electrodes with the loading of ~1.5 mAh/cm2 demonstrated ~92% capacity retention over 300 cycles. The composite electrodes of porous Si and graphite (~3 mAh/cm2 loading) with a specific capacity of ~650 mAh/g demonstrate ~82% capacity retention over 450 cycles. In another effort, hierarchical structured Si/CNT microspheres developed not only have good porous structure to accommodate the volume expansion and achieve ~30% apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to ~200 MPa pressure. The anodes deliver a high specific capacity of ~1500 mAh/g and 85% capacity retention over 200 cycles at the areal loading of ~3 mAh/cm2.

4:15 PM QN08.02.06 Metal Amidinate Precursors for General Solution-Phase Synthesis of Intermetallic Nanocrystals Andrew J. McGrath1, Filip Ronning and Sergei A. Ivanov; Los Alamos National Laboratory, Albuquerque, New Mexico, United States.

Nanocrystalline intermetallic compounds show promise in several applications, however chemical methods giving phase purity and size control are lacking. Using metal precursors previously developed for atomic layer deposition but rarely explored for solution-phase materials synthesis, we demonstrate the synthesis of several phase-pure transition metal alloys including the full library of MSn; and MSb (M = Cr, Mn, Fe, Co, Ni) with control over phase and stoichiometry, several of which are reported for the first time in nanocrystalline form. For stannides, the synthesis of which occurs above the melting point of Sn, the alloys formation progresses via an intermediate stage of small Sn nanocrystals stabilized by the strongly-binding amidinate ligands with subsequent diffusion of transition metal atoms into tin. We find that for metals with higher melting temperatures than Sn (such as Sb), the reductant injection temperature determines the phase purity of the intermetallic product. Temperature-dependent magnetic properties of the intermetallic nanocrystals have been studied, and the effect of annealing the nanocrystals at high temperatures on crystallinity is also explored.

4:30 PM QN08.02.07 Colloidal Quantum Dot Lasing with Sub-Single-Exciton Thresholds Using Second-Order Distributed Feedback Resonators Young-Shin Park1,2, Jeongkyun Roh1, Oleg

Ziha1,2; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); 2Korea Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

Our laboratory has developed a new synthetic procedure for generating periodic arrays of metallic nanostructures shaped as hexagonal or triangular nanoplates using a room temperature light-activated growth mode. Such structures have the potential to act as interactive components for the detection of biological and chemical analytes using various sensing modalities (e.g., Surface Enhanced Raman Scattering (SERS)). The synthesis is reliant on the formation of Au seeds exhibiting planar defects – without such defects the growth mode is deactivated. Through the engineering of defects, which have been extensively studied using Titan TEM imaging and electron diffraction, such structures have now and achieve ~30% apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to ~200 MPa pressure. The anodes deliver a high specific capacity of ~1500 mAh/g and 85% capacity retention over 200 cycles at the areal loading of ~3 mAh/cm2.
Colloidal semiconductor quantum dots (QDs) are attractive materials for application as laser media because of their high photoluminescence (PL) quantum yields, size-tunable emission colors, and amenability to solution-based processing. Optical amplification in these materials is hampered by nonradiative Auger recombination of gain-active multicharacter states. Recently, we have demonstrated that this problem can be successively addressed by interface-engineering in hetero-structured, compositionally graded QDs. Using these novel structures, we were able to demonstrate both low-threshold lasing with pulsed optical excitation as well as optical gain with d.c. electrical pumping (Nat. Mater. 17, 42. 2018). The next step on the way to practically realizing a QD laser diode is incorporation of a proper feedback system into a high-current-density light-emitting diode (LED).

Towards this goal, we investigate optical properties of photonic structures comprised of a one-dimensional distributed feedback (DFB) resonator and the newest generation of the QD with strongly suppressed Auger decay. These QDs have a CdSe core (~ 2 nm radius) enclosed into a radially graded CdZnS,Se layer (~ 5 nm thickness), completed with a final protective thin (< 1 nm) shell of ZnSe. These structures show a high biexciton PL quantum yield of ~ 45%, which is a result of an exceptionally long biexciton Auger lifetime of > 2ns. QDs are spin-coated onto a DFB produced into the SiO2 substrate via laser interferometric lithography. The grating parameters (pitch, duty cycle, and depth) are selected so as to provide optimal conditions for surface-emitting lasing with the second-order in-plane optical feedback. Applying a Fourier-plane angle-resolved spectroscopy for the analysis of surface lasing produced by the first-order Bragg scattering, we observe that our QD-DFB structures are characterized by an X-shaped photonic mode dispersion. In particular, we detect a ca. 10 nm stop band in the direction normal to the DFB plane which indicates strong optical feedback between counter-propagating in-plane modes (coupling coefficient of ~20), a key to obtaining low-threshold lasing. The fabricated structures also exhibit a fairly high quality factor of ~ 600.

Using optical excitation with 400 nm, 100-fs laser pulses, we observe single-mode lasing at the lower-energy edge of the stop band of the TE mode, which corresponds to reduced losses via surface emission due to a destructive character of interference between in-plane counter-propagating waves. The measured thresholds are consistently below 10 μJ/cm², and the lowest value is ~ 5 μJ/cm². To further lower the lasing thresholds, we apply ideas of “zero-threshold gain” by photo-chemically doping the QDs, which suppresses losses due to ground-state absorption (Nat. Nanotechn. 12, 1140. 2017). Using this approach, we are able to reduce lasing thresholds to the unprecedented level of ~2 μJ/cm², which corresponds to excitation of only ~0.3 exciton per QD on average. This is a 3-fold reduction compared to the fundamental one-exciton-per-dot limit in the case of the undoped QDs. In our ongoing work, we investigate lasing properties of similar DFB resonators incorporated into state-of-the-art QD-LED stacks.

References

SESSION QN08.03: Nanoparticle Synthesis and Applications II
Session Chair: Hongyou Fan
Tuesday Morning, April 23, 2019
PCC North, 100 Level, Room 129 B

10:30 AM *QN08.03.01
Surface Chemistry of Colloidal Cesium Lead Halides Nanocrystals
Maryna Bodnarchuk1, Simon Böhme2, Ivan Infante1 and Maksym V. Kovalenko1,2,3
1Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; 2ETH Zürich, Zürich, Switzerland; 3University of Amsterdam, Amsterdam, Netherlands.

Colloidal organic/inorganic lead halide perovskite nanocrystals (NCs) are intensely pursued as highly promising, low-cost light-emitting materials with wide color gamut. These NCs exhibit unprecedented luminescent properties – narrow-band emission with high quantum efficiency, covering the whole visible spectral range and extending into near-infrared, all obtained without epilayer overcoating of the NC surfaces for electronic passivation of the surface states [1]. Their processing and luminescent properties are challenged by the lability of their surfaces, i.e. the interface of the NC core and the ligand shell. Surface and sub-surface atoms are likely directly involved in all possible chemistry equilibria and transformations. Controlling NC surface structure is therefore paramount for mitigating these instabilities. On the example of CsPbBr3 NCs, we rationalize the typical observation of a degraded luminescence upon aging or the luminescence recovery upon post-synthesis surface treatments using a simple surface-structure model, supported by DFT calculations [2]. Healing of the surface trap states requires restoration of all damaged PbX octahedra and establishing a stable outer ligand shell. Such NCs are halogen-rich. Restoration of such a structure, seen as an increase in the luminescence quantum efficiency to 90-100% and improvement in the overall robustness of CsPbBr3 NCs, was attained using a facile post-synthetic treatment with a PbBr2+DDAB (didodecyldimethylammonium bromide) mixture. In practical terms, we demonstrate that such an approach is useful to obtain purified CsPbBr3 NCs samples, washed up to three times in several solvents, with near unity photoluminescence quantum yields and long-term colloidal stability.


11:00 AM *QN08.03.02
Shape and Surface Patchiness Directed Nanoparticle Superlattice Assembly Revealed by Liquid-Phase Transmission Electron Microscopy
Qian Chen; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

We utilize the combined toolset of low-dose liquid-phase transmission electron microscopy and automated single particle tracking to reveal the fundamental crystallization pathways in nanoparticle superlattice formation. We concern nanoparticle systems involving systematically-changing shapes and surface patchiness, which give rise to a rich diversity of crystallization behaviors, such as hierarchical crystallization, layer-by-layer growth, polymorph interconversion as well as corner-connected open lattice formation. Such behaviors hinge on the specific length scale and time scale of nanoparticle motions, which can be potentially generalizable to the phase behaviors of other nano-sized systems in solution.
Metal-oxide nanocrystals doped with alienvalent atoms can exhibit localized surface plasmon resonances (LSPRs) that are tunable across the infrared regions of the electromagnetic spectrum. Yet, the chemical identity and the maximum concentration of active dopants for any specific metal-oxide nanocrystal have remained limited, which is largely due to the difficulty in establishing reaction kinetics that favors dopant incorporation with the widely used co-thermolysis method. In this presentation, I will share our recently developed ion-exchange method for the incorporation of various cationic dopants into preformed metal-oxide nanocrystals while preserving their size, shape and crystal structure. We show that successful addition of p-type dopants into n-type metal-oxide nanocrystals, which may not be feasible using alternative synthetic methods, leads to programmable LSPR redshifts by virtue of dopant compensation. We further demonstrate that enhanced n-type doping can be realized via rationally designed sequential cation-exchange reactions, yielding metal-oxide nanocrystals with the ensemble LSPR energy surpassing that of beginning nanocrystals. Our work shows that ion-exchange transformations can add a new dimension to the chemical design of infrared plasmonic nanocrystals, allowing metal-oxide nanocrystals synthesized by existing methods to be used as templates to create compositionally tunable nanocrystals with well-defined LSPR characteristics.

Quantum confined semiconductor nanocrystals have been widely investigated as light harvesting and charge separation components in photovoltaic and photocatalytic devices. The efficiency of these semiconductor nanocrystal-based devices depends on many processes, including light harvesting, carrier relaxation, charge separation and charge recombination. The competition between these processes determines the overall solar energy conversion (solar to electricity or fuel) efficiency. Compared with single component quantum dots (QDs), semiconductor nanoheterostructures, combining two or more materials, offer additional opportunities to control their charge separation properties by tailoring their compositions and dimensions through relative alignment of conduction and valence bands. Further integration of catalysts (heterogeneous or homogeneous) to these materials form multifunctional nanoheterostructures. Using Pt tipped CdSe/CdS dot-in-nanorods(NRs) and CdS nanoplatelets as model systems for 1D and 2D heterostructures, we are examining the mechanism of long-lived charge separation and H₂ generation in the presence of sacrificial electron donor. The rates of carrier transport, interfacial charge (electron and hole) transfer, and charge recombination can be directly monitored by transient absorption and time-resolved fluorescence spectroscopy. In this talk, we will discuss how the rates of these elementary carrier transfer and transport processes depend on the dimension (size and length), morphology and band alignment in these materials, affect the overall H₂ generation efficiency and can be optimized through rational material design.
harvest high quality supercrystals with desired superlattices.

4:00 PM QN08.04.05
Electronic, Optical and Transport Properties of PbS Nanocrystal Superlattices Yun Liu, Nolan Peard and Jeffrey C. Grossman; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Optoelectronic devices made from colloidal quantum dots (CQDs) often take advantage of the combination of tunable quantum confined optical and electronic properties and carrier mobilities of strongly coupled systems. For lattices of connected CQDs, of interest is the interplay between confinement effects and band-like behavior. In this work, first-principles calculations are applied to investigate the electronic, optical and transport properties of PbS CQD superlattices. Our results show that even in the regime of strong necking and fusing between CQDs, quantum confinement can be generally preserved. In the bandlike regime, computed carrier mobilities for simple cubic and 2D square lattices fused along the [100] facets are 2-4 orders of magnitude larger than those of superlattices fused along other [110] and [111] facets. The relative magnitude of the electron and hole mobilities strongly depends on the crystal and electronic structures. We also find that the carrier mobilities of CQD solids increases as the size of the quantum dot increases due to the stronger coupling between neighboring nanocrystals. Our results illustrate the importance of understanding the effects of crystal structure and connectivity of CQD films.

4:15 PM QN08.04.06
Computational Design of Nanoparticles with Tunable Water-Mediated Interactions Reid Van Lehn; University of Wisconsin–Madison, Madison, Wisconsin, United States.

Functionalized, monolayer-protected nanoparticles (NPs) are versatile materials with surface properties that depend on monolayer composition. Ultrasmall gold NPs (<10 nm in diameter) are of particular interest for drug delivery applications because their small size enables unique interactions with serum proteins and the cell membrane. However, structure-property-interaction relationships correlating NP compositions with their biological interactions remain unclear and can be challenging to determine experimentally.

Here, we present molecular simulation approaches from our group that can guide the design of NP monolayer compositions for biomedical applications. Motivated by prior work that identified NP hydrophobicity as a key parameter driving cellular internalization and protein adsorption, we use atomistic molecular dynamics simulations to quantify NP hydrophobicity as a function of monolayer physical and chemical properties. These results demonstrate how the cooperative interactions of collections of surface-grafted molecules contribute to spatially varying hydrophobic interactions with homogeneous monolayers. We further show that hydrophobic interactions at uniformly nonpolar interfaces can vary in magnitude depending on the fluctuations of surface-grafted alkanethiol ligands, and that these same fluctuations depend on NP core size and shape. These results are further confirmed by atomic force microscopy experiments. Finally, we present a new deep learning methodology to rapidly screen the hydrophobicity of NPs as a function of monolayer composition using only minimal simulation input. This mechanistic insight and new computational tools can be leveraged to design NPs with desired surface properties.

4:30 PM QN08.04.07
In-situ Atomic-Scale Observation of Kinetic Pathways of Sublimation in Silver Nanoparticles Leonard D. Francis; Department of Advanced Electron Microscopy, Imaging and Spectroscopy, International Iberian Nanotechnology Laboratory, Braga, Portugal.

The process by which a crystal sublimes into a gas is a first-order phase transition of considerable fundamental and practical importance in condensed-matter physics, material science and climate change, yet a detailed understanding of its relevant kinetic pathways is still evolving even for the model systems whose equilibrium configuration is known in advance.1 Transmission electron microscopy (TEM) in principle, enables us to observe dynamic process directly, yet to date many of the TEM studies on sublimation dynamics have been implemented on nanostructures at the nanometer scale, such as nanowires, nanorods and colloidal nanocrystals.2 Observing sublimation at the atomic scale has been mostly performed recently on two dimensional layered materials owing to their suitable thickness as a TEM sample in order to exclude the projection issues in electron microscopy. In case of metals, silver (Ag) nanocrystals with a face-centred cubic (FCC) structure show a low sublimation temperature.3 As such, Ag represents an ideal model material to track heating induced sublimation procedure inside an electron microscope. Nevertheless, due to the limit of spatial resolution of a conventional TEM, many critical details such as structural evolution, dynamic processes, sublimation mechanisms and role of defects during sublimation remain unclear as well as not very well established at the atomic scale. With the development of aberration-corrected TEM (AC-TEM) and advanced heating stage, in-situ dynamic observations at atomic resolution can be achieved even at a low voltage, allowing us to directly resolve extremely small nanostructures that are not clearly visible by a conventional TEM.

Here, we report the in-situ atomic-scale observation of the sublimation dynamics of Ag nanoparticles with a size smaller than ~30 nm under heating conditions using an advanced heating holder within an AC-TEM. The Ag nanoparticles are fabricated directly on the TEM heating chips by plasma irradiation in vacuum system to avoid unwanted solvent effects, and both plan-view and cross-section view of the sublimation dynamics are implemented at the atomic scale. We find surprisingly that the sublimation and atomic rearrangement coexist in small Ag nanocrystals during heating and reveal that the sublimation-induced stable surfaces are the low-energy [111] and [100] planes for the Ag nanocrystal with a size smaller than ~30 nm. In addition to the size-dependent sublimation behaviors, we also demonstrate that surface energy and defects are also of relevance in determining the sublimation pathways, i.e. the Ag nanoparticles of a low surface energy show a uniform sublimation pathway, while those of a high energy or 5-fold twin grain nanocrystal with a size smaller than ~30 nm. In addition to the size-dependent sublimation behaviors, we also demonstrate that surfactant energy and defects are also of relevance in determining the structural evolution, dynamic processes, sublimation mechanisms and role of defects during sublimation remain unclear as well as not very well established at the atomic scale.

4:45 PM QN08.04.08
Superlattice Nucleation and Underlying Mechanism of Magnetcite Nanocube Assembly Xin Huang and Zhongwu Wang; Cornell University, Ithaca, New York, United States.

The self-assembly of colloidal nanoparticles into ordered superlattices provides significant expansions for the capability of functional materials design. As the new type of building blocks, the geometric shapes of nanocrystals, such as sphere, cube and octahedron, play critical roles in determining the structure of assembled supercrystal. In the nanocube system, the observed superlattices were dominated by the three phases of simple cubic (SC), rhombohedral (Rh), and face-centered cubic (FCC), but how they nucleate and grow and from one to another remain largely unknown. In this work, we applied highly monodisperse magnetite nanocubes with an average side length of 12.5 nm, and controlled various assembly environments, and revealed the formation and growth of three major phases (SC, Rh and FCC). Taking advantage of synchrotron-based SAXS techniques, we also explored the structural correlations between these superlattices phases. With additional simulations and computations, we further discussed the driving forces and constructed a reasonable superlattice phase diagram of nanocube-based assembly. Our results not only dramatically expand our understanding of the shape-dependent phase behaviors of nanocrystal, but also provide insights for design and fabrication of novel functional materials.

Session Chairs: Mei Cai, Hongyou Fan, Yu Han and Han Htoon
Tuesday, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

Session QN08.05: Poster Session I: Colloidal Nanoparticle

QN08.05.01
Molecular Control over the Composition of Solid/Solid Interfaces within Nanocrystal Solids Obtained from Colloidal Nanocrystals Santosh Shaw², Tiago F. Silva¹, Jonathan M. Bobbitt³, ⁴, Fabian Naab⁵, Cleber L. Rodrigues¹, Bin Yuan⁶, Julia J. Chang⁷, Xinchun Tian⁸, Emily A. Smith⁹ and Ludovico Cademartiri², ⁴, ⁸; ¹Instituto de Física da Universidade de São Paulo, São Paulo, Brazil; ²Materials Science & Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; ³Chemistry, Iowa
State University of Science and Technology, Ames, Iowa, United States; 2US Department of Energy, Ames Laboratory, Ames, Iowa, United States; 3Michigan Ion Beam Laboratory, University of Michigan, Ann Arbor, Michigan, United States; 4Chemical & Biological Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

We will describe a bottom-up approach to the control of the composition of solid/solid interfaces in nanostructured materials obtained from colloidal nanocrystals. Leveraging the highly selective removal of organics by plasma processing we show that introducing inorganic elements in the ligands of the starting building blocks allows for controlling the interfacial composition of the final all-inorganic ligand-free nanostructured film. We compare the results from ZrO₂ colloidal nanocrystals capped with trioctylphosphine oxide (TOPO) or oleic acid (OA). The interfaces in the plasma processed all-inorganic colloidal nanocrystal assemblies (CNAs) are either nearly bare (for OA-capped nanocrystals) or are terminated with phosphate groups (for TOPO-capped nanocrystals) resulting from the reaction of phosphate oxide groups with plasma species. This modification of the composition of the interfaces has extensive effects on the properties of the material: (i) different growth kinetics indicate different rate limiting processes of growth (surface diffusion for the phosphate-terminated surfaces and dissolution for the “bare” surfaces); (ii) different activation energies of growth indicate three-fold change in interfacial energy; (iii) different phase transformation temperatures show that surface modifications can stabilize the tetragonal phase of ZrO₂ at 900°C without the need for doping.

QN08.05.02

Fluorescent Silver Nanoclusters for Rapid Detection of Pathogenic DNA Yuxiang Chen¹, Peter Goodwin¹ and Jennifer Martinez²; ¹Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ²Department of Chemistry, Northern Arizona University, Flagstaff, Arizona, United States.

DNA-templated silver nanoclusters (Ag NCs) have recently attracted significant research attentions due to their intriguing fluorescent properties, especially in the arena of biosensing and bioimaging. Compared to other widely used fluorescent probes, such as organic dyes, quantum dots, and metal nanoparticles, fluorescent Ag NCs show unique advantages including high photo-stability, low toxicity, and high fluorescent quantum yield, etc. In this poster, we will present a new fluorescent assay platform for the rapid and selective detection of pathogenic DNA sequences using a common foodborne pathogen, i.e. *Listeria*, as the target. In addition, this potentially versatile NCB based platform can be extended to detect other pathogens and bacteria strains at a point-of-care setting.

QN08.05.03

Ink Formulation, Surface Tension Control, and Optimal Microscale Printing of CdSe Quantum Dot Dispersion for Efficient Light Emitting Diode Array Ji-hye Kim, Seok-Ho Hwang, Ohyoung Kim and Byung Do Chon; Dankook University, Yongin, Korea (the Republic of).

Quantum dot light-emitting diodes (QD-LEDs) is a next-generation display technology with narrow-band, highly efficient and widely tunable emission. For a large area compatible patterning of QD-LEDs, solution process such as inkjet printing is promising but relatively complicated parameters exist. For example, quantum dot nanoparticle dispersion in a common solvent produces a non-uniform dried surface as well as strong coffee-ring at edge boundaries. Therefore, uniform filling of a confined light emitting pixel geometry is difficult. Using the mixture of various solvents such as 1,2,4-trimethylbenzene, anisole, and cyclohexylbenzene, giant effectiveness of ink jetting can be achieved. However, the redox of coffee-ring effect at edge boundaries can sometimes accompanies poor surface morphology. We have controlled the solid contents of CdSe nanoparticles at the condition of proper mixture solvents; addition of small amount of high viscosity and high boiling point solvent was effective method. Evaluation of the printed patterns including a dot/line size variation as well as surface morphology were linked with resultant device efficiency (ITO/PEDOT:PPy-TOP/CdSe quantum dot/ZnO/LiF/Al) for different solid contents of CdSe in inks. Fine-line microscale patterned quantum dot LED (line patterns of 80/120 micrometer linewidth/subpixel pitch; 165dpi and more precise pattern) could be fabricated on the photoresist-processed bank test QD-LED cells.

QN08.05.04

Controlled Fragmentation of Quasi-Infinite Particle Chains into Oligomeric Subchains Under the Influence of External Strain Anja Maria Steiner¹, Martin Mayer¹, Maximilian Seuss¹, Tobias A. König¹,² and Andreas Ferti¹,²; ¹Institute of Physical Chemistry and Polymer Physics, Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany; ²Physical Chemistry of Polymeric Materials, TU Dresden, Dresden, Germany.

Among the different plasmonically active assemblies, linear chains of nanoparticles are of special interest. These plasmonic polymers can provide directional, plasmonic waveguiding properties, as well as polarization-dependent field enhancement. An essential parameter governing many optical effects is the number of particles (n) forming a chain. Above the so called infinite chain limit, n, the dependence of plasmonic properties is limited; however, shorter chains below n=1 (i.e., plasmonic oligomers) are highly responsive to variations in n. Therefore, controlling n below the infinite chain limit is an active topic in nanophotonics. We present a scalable approach towards the formation of oriented chains consisting of a few plasmonic nanoparticles, according to the described plasmonic oligomers. These plasmonic oligomers are formed by first assembling quasi-infinite chains above the infinite chain limit and subsequently fragmenting them using mechanical deformation of the underlying elastomeric substrate. Detailed studies of the fragmentation process from quasi-infinite chains are conducted by UV–-vis–NIR spectroscopy and in situ atomic force microscopy (AFM). [2] By evaluation of the strain dependent optical properties, we observed a reversible, non-linear shift of the dominant plasmonic resonance. Using electromagnetic simulations, the optical spectra were deconvoluted into the corresponding ensemble of oligomers that correspond to the oligomer length distribution and dispersity yielded from the AFM measurements. Based on the obtained experimental results and mechanical simulations computed by the lattice spring model, we proposed a formation mechanism that explained the observed decrease of chain polydispersity upon increasing strain and provided experimental guidelines in tailoring chain length distribution. Furthermore, we also demonstrated that the chain length can be tuned depending on the ratio of cohesion between the particles and adhesion of the colloids to the supporting elastomeric substrate. In this work, we demonstrate, that mechanical stress is a powerful tool for the scalable fabrication of oriented linear plasmonic oligomers and opens new avenues for strain-dependent optical devices and mechanophotonic applications. An example is surface-enhanced sensing, where the reversible switching of the nanostructure may be utilized to trap/infiltrate target molecules into uniform hot-spots


QN08.05.05

Non-Classical Crystallization Mechanisms During the Synthesis of PbS Colloidal Nanocrystals Bin Yuan¹ and Ludovico Cademartiri¹; ¹Materials Science and Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; ²Ames Laboratory, Ames, Iowa, United States; ³Chemical and Biological Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States.

One of the two main classes of mechanisms generally used to explain the formation of nanocrystals is the non-classical aggregative growth (e.g. oriented attachment, step-growth crystallization). Better understanding of these mechanisms should enable better control over the size, shape, and monodispersity of the products. Even though great strides have been made in using the aggregative growth mechanism to synthesize novel nanostructures (e.g. nanorings, ultrathin nanowires) and in visualizing the process in real time with liquid TEM since the seminal work Penn and Banfield on oriented attachment, there is still a long way to go towards understanding this process mechanistically. Two major roadblocks are (i) establishing a model reaction system that only involves the aggregative growth (meaning that classical growth mechanisms are not happening or negligible) and (ii) collecting the kinetic data (i.e. size and concentration of each individual population vs time) quantitatively. We will show how we have overcome the two abovementioned roadblocks by using PbS nanocrystals synthesized by a highly reactive sulfur precursor. This system shows no detectable Ostwald ripening or classical supersaturation-induced growth, and allows for the optical characterization of the individual populations. We show that modeling the aggregative growth kinetics in this system require two separate mechanisms, one whose activation energy is proportional to the radius of the particles and one that is proportional to the volume of the particles. We will then describe how these two mechanisms can be explained within the framework of oriented attachment.
Ceria nanoparticles are used to polish silica due to their high oxide removal rate without the need for added chemicals. Since the early 20th century, ceria has been used to polish glass lenses, and more recently thermal oxides during semiconductor chip fabrication. This second application benefits not only from a high removal rate but also from a high selectivity relative to nitriles. Both of these features are a result of a reversible redox reaction at the surface of the particles allowing them to participate in polishing through both mechanical and chemical means. Ceria’s ability to undergo this reaction is governed by the ratio of Ce⁴⁺/Ce³⁺ on the surface of the particles. As this ratio increases, the interaction with the silica surface, resulting in an increased removal rate. This ratio can be affected by both physical factors such as particle size and synthesis conditions, and chemical factors such as interactions with other slurry components. In this study, glass and thermal oxides were polished on a benchtop polisher and the removal rates were determined using a profilometer and ellipsometer respectively. Model slurries with oxidation state ratios between 5% and 25% were prepared by varying the oxidizing agent and surfactant concentrations as well as the surfactant type. A ceria slurry currently being used in industrial thermal oxide polishing was obtained as a reference (oxidation state ratio of 4%) and a silica slurry was used as a pure mechanical removal control. All the ceria slurries tested had a greater removal rate than the silica slurry, even at low oxidation state ratio. The greatest removal rate was found for the model slurry with 24% Ce⁴⁺ on the particle surfaces, resulting in removal rates at least 1.5 times those of the commercial slurry and 3 times those of the silica slurry for both materials. We discuss these findings and their implications for the specific design of future slurries.

Sodium is necessary for regulating osmotic pressure and assisting the operation of nerve, heart, muscle and various physiological functions in the body. Sodium intake is mainly through food, especially salt. However, excessive sodium intake is harmful because it may lead to the high risk of heart attack, stroke and the development of cardiovascular disease. For the above-mentioned reasons, we worked on developing a rapid, reliable, and sensitive method to detect salt concentration which can be directly monitored by naked eyes. In this study, we utilize the gold nanoparticles (AuNPs) as the colorimetric sensor due to the remarkable characteristic of localized surface plasmon resonance (LSPR) at visible wavelength regions. Based on the concept of LSPR effect, the designed AuNP-based sensor can readily monitor the change of salt concentrations through the color change observed by naked eyes. This phenomenon can be attributed to the ion-induced aggregation of AuNPs, where the response time relative to the salt concentrations can be modulated with the proper control of related detection conditions. Furthermore, in order to improve their detection sensitivity, the organic compound was utilized to further modify the surfaces of AuNPs, and can efficiently reduce the reaction time for readily identifying the biological and chemical sensing applications.

Over the past few decades, the development of rare earth (RE) based light emitting diodes (LEDs) has revolutionized the solid-state lighting industry due to the unique optical and electronic properties of RE elements. The RE luminescence in LED phosphors is often amplified via co-doping with a sensitizer agent (Ce³⁺, Yb³⁺) and/or coating a shell layer for surface passivation. However, there has been a huge push to replace the RE elements in these materials due to their rarity and high demand. Therefore, to sustain energy efficient LED lighting, earth abundant transition metal (TM) elements are being proposed as replacements to RE sensitizers owing to their large absorption cross-sections. Despite their susceptible nature, there is motivation to use TM sensitizers to design tunable luminescent phosphors through the energy coupling of RE-TM ions. The current project demonstrates the ability to tune the optical properties of upconversion phosphors, allowing for controlled absorption and emission spectra in RE doped core-TM doped shell phosphors. In this work, hexagonal β-NaYF₃:Er³⁺/core nanoparticles (NPs) were synthesized with different wet chemistry techniques such as hydrothermal, colloidal synthesis, etc. with controlled sizes, and TiO₂:Ni²⁺ shell layer was deposited via sol-gel chemistry. Initial optoelectronic (UV-Vis, and XPS) and structural (XRD) characterizations were performed on TiO₂:Ni⁴⁺ NPs to identify the optical absorption spectra, oxidation states, and crystal structure. The surface of TiO₂:Ni⁴⁺ NPs was functionalized with para-substituted benzoic acid ligands to demonstrate controlled optoelectronic properties of the TM dopant (Ni³⁺) in a solid host (TiO₂) by modifying the surface dipole by up to 9.5 D. The local structural and electronic changes around Ni³⁺ with the ligand were investigated via time-of-flight neutron scattering (NS) and soft x-ray absorption spectroscopy (XAS), respectively. The atomic pair distribution function (PDF) analysis of the NS data and the intensity ratio of t₂g-eg peaks in N₁ L-edge XAS spectra indicate that the local geometry distortion is accompanied by a change in the electron density in the valence orbitals (3d) of Ni²⁺. These adaptive optoelectronic properties of Ni²⁺ with surface ligands was coupled with the steady emissions of Er³⁺ in NaYF₃:Er³⁺/TiO₂:Ni⁴⁺ core-shell NPs to systematically tune the luminescence of the core-shell phosphor. The ligand induced shifts in the optical absorption (~ 50 nm) and emission spectra of these phosphors were determined by UV-Vis and photoluminescence (PL) measurements. Additionally, the excited state energy transfer kinetics between the RE-TM ion couple were extracted from the life-time decay measurements, which will assist in the development of TM sensitized RE phosphors. These adaptive luminescent phosphors will positively influence the solid-state lighting applications by reducing the RE dependence in LEDs, anti-counterfeit technologies, bio-detection etc.

Colloidal quantum dots (QDs) that are partially fused together to form highly-carried, highly-ordered superlattices (SLs) are an exciting new class of materials for optoelectronics. These **epitaxially-fused** QD SLs promise to combine the band-like carrier transport of bulk semiconductors with the size-tunable photophysics and solution processability of QDs. However, the structure and formation mechanism of these QD SLs are poorly understood, which limits our ability to fabricate high-performance QD SLs with controlled electronic properties.

In this talk, I present a novel combination of X-ray scattering and correlated electron imaging and diffraction used to rigorously determine the superlattice unit cell of oleate-capped QDs (oleate-SLs) and QD slurry particles. This “dual space” method is a powerful and general way to unambiguously assign the structure of 3D colloidal SLs at the single grain level. We find that oleate-SLs fabricated through self-assembly on a liquid substrate adopt a trigonally-distorted body-centered cubic structure with two major out-of-plane SL orientations. I show that the QDs have full orientational as well as positional order in this structure and that both the lateral size of the SL grains and their degree of distortion from true bcc depend on ligand coverage. The two orientations of oleate-SL grains convert to two distinct orientations of the epi-SL with a very different appearance in the electron microscope. The phase transition occurs almost purely via the 3D QDs with minimal rotational motion, resulting in a trigonally-distorted simple cubic epi-SL with fusion along the PhSe₁₀₀ facets. This simple translational phase transition is made possible by the trigonal distortion of the initial oleate-SL and results in ~5 μm epi-SL grains free of linear or planar defects. The ligand content, elemental distribution, and impact of atomic layer deposition infilling on the structure of the epi-SLs will also be highlighted. The powerful correlated imaging and diffraction methodology presented here will help enable detailed understanding of complex nanomaterial superstructures. Furthermore, we show that small distortions in the oleate-SL structure have important ramifications on the epi-SL phase transition and the ability to make highly-perfect epitaxially-fused QD superlattices.
the dried NPs. This renders deposited ink non-conductive unless additionally treated after deposition. In order to ensure metal-metal contact and conductivity, ligands have to be removed by sintering that is incompatible with many substrates [1]. In order to avoid this, we developed hybrid NPs that combine gold metal cores and conjugated polymer shells that we will briefly introduce in this talk. Their synthesis is based on a ligand exchange reaction of cetyltrimethylammonium bromide (CTAB) capped gold nanorods (AuNRs) by conjugated polymers such as poly[(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PPS) and poly[2-(3-thienyl)-ethoxy]-4-butylylsulfonate] (PTESBS). The hybrid particle design allows good electron transport upon ink drying, rendering sintering unnecessary. After deposition, dry films of hybrid NP inks exhibit conductivity on the order of 1.0 x 10⁴ S/m. We used infrared (IR) and Raman spectroscopy to demonstrate the successful ligand exchange and to investigate how metal core interact with polymers and how different particles connect. These polymers serve as ligands and confer high colloidal stability to particles in water and other solvents, too, enabling advanced ink formulations. The resulting inks exhibited good stability of at least one year at high gold concentration of 200 mg/mL [1].

Here, we present an extension of the sinter-free hybrid ink concept to core materials and shapes beyond the gold nanorods mentioned above. First, we discuss the large-scale production at high concentrations of faceted gold NPs with diameters below 100 nm. In order to control the coalescence process and avoid the NPs aggregation, we used plant extracts and infusions to synthesize metal and metal oxide NPs. Due to the simplicity and eco-friendliness of these methods, metal and metal oxide NPs synthesis using plant extracts and infusions has been widely used. The most common methods are based on the reduction of metal ions with organic compounds such as plant extracts or infusions. These methods are easy to use, do not require complex equipment, and are sustainable. However, the size and morphology of the NPs are not always well controlled. To overcome this limitation, we use a combination of plant extracts and infusions with metal solutions. This approach allows us to control the size and shape of the NPs, as well as their composition, and to achieve a high degree of monodispersity. The use of plant extracts and infusions as reducing and stabilizing agents is a promising approach for the synthesis of metal and metal oxide NPs with specific properties. These NPs have potential applications in various fields, such as catalysis, sensors, and energy devices. In our research, we have focused on the synthesis of silver and copper NPs using organic molecules as reducing and passivating agents. These NPs have shown promising properties for applications in water purification, drug delivery, and photovoltaics. We have also investigated the use of these NPs in the development of hybrid inks for inkjet printing. Our hybrid inks exhibit high colloidal stability, good conductivity, and a wide range of optical properties. These inks have potential applications in printed electronics, where they can be used for the fabrication of devices with high performance and low cost.
Facile, Green Synthesis of Cerium/Vanadate Oxide Nanoparticles—Biomedical and Electrochemical Application

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Nanoscale cerium oxide has shown high catalytic activity towards numerous substrates in applications relevant to the chemical and biomedical industries. The utility of this material derives from the Ce4+/Ce3+ redox couple and surface oxygen defects, with the material's broad applicability across industries arising from the ability to tune surface defect concentrations via synthesis approach. Despite ceria’s high catalytic activity and efficiency: the material’s cost/scarcity may limit its use in industry. The present work focuses on a facile, green synthesis incorporating vanadium into ceria nanoparticles as a means to reduce the cost of catalyst materials, without sacrificing efficiency, while increasing the potential application space. Ultra-small, stable (hydrodynamic radius: 22 nm; zeta potential: 28 mV) cerium/vanadium oxide nanoparticles are produced via hydrolysis through the mixing of cerium and vanadate (as an inorganic redox agent) pre-cursors in water. The particles were washed to remove residual reagents and used without further modifications. The particles were deposited on glassy carbon electrodes and tested using cyclic voltammetry, chronocoulometry, and linear sweep voltammetry to detect various bio-molecules and as a pseudocapacitive material. Further, synthesis parameters were optimized and tested for enzyme-mimetic activity against comparable cerium oxide nanomaterials in standard chemical assays. This material demonstrates high catalytic activity in biomedical and electrochemical applications through a simple green synthesis method while reducing synthesis cost by limiting cerium fraction.

QN08.05.15

Using Quantum Dots in a Sol-Gel Matrix to Enable Deep UV Imaging for Silicon Based Detectors

Alex Knowles1, Scott Williams1, Zoran Ninkov2 and Ross Robinson1; 1College of Science, Rochester Institute of Technology, Rochester, New York, United States; 2Center for Imaging Science, Rochester Institute of Technology, Rochester, New York, United States.

CdSe/ZnS quantum dot (QD) incorporation into a sol-gel matrix that forms a deep UUV transparent thin film window will be presented. Silicon-based CMOS and CCD detectors coated with a thick Lumogen layer is the current state of the art in detector high-energy sensitization. QDs, however, may provide enhanced advantages over Lumogen, such as tunable emission wavelength, lower production costs, and a greater range of solvent choices. We have demonstrated that CdSe/ZnS quantum dots synthesized with polar solvent dispersible ligands enables formulation of ink jet printable inks. To achieve the film thicknesses required for high quantum yield detector sensitization, we have introduced sol-gel chemistry into the ink formulation to produce highly transparent UUV transmissive thick film windows. Implementation of MgF2 will be reported. Performance characterization using scanning electron microscopy, vacuum-ultraviolet absorption spectroscopy, and quantum yield will be presented.

QN08.05.16

Effect of Zn Precursor Concentration on the Blinking Behavior of CuInS2/ZnS Quantum Dots and Characterization of Fast Blinking Particles for Super-Resolution Imaging

Anh Nguyen and Colin Heyes; Arkansas University, Fayetteville, Arkansas, United States.

Cadmium-free CuInS2/ZnS core/shell quantum dots are synthesized through a non-injection synthetic method for both the cores and shelling steps. The resulting CuInS2/ZnS quantum dots are small (~4–7 nm) and spherical with photoluminescence quantum yields (PLQY) in the range of 40–70%. The structure, chemical composition and optical properties of CuInS2/ZnS quantum dots at both ensemble and single-particle level are carefully investigated as functions of the synthesis conditions. The results show that overcoating CuInS2 cores using relatively low amounts (0.1 mmol) of Zn(S2)2 precursor during the shelling step leads to an extensive cation exchange process that forms an alloyed core, followed by a thin ZnS shell that significantly increases the quantum yield. Increasing the amount of Zn(S2)2 to 2-4 mmol during shelling leads to more extensive cation exchange/alloying as well as forming thicker shells. Using higher amounts of Zn reduces the QY compared to using lower amounts of Zn, but the fluorescence intermittency (blinking) is significantly reduced. Moreover, we use a single particle subpopulation analysis to gain a better comprehension of the ion exchange/alloying/shelling processes and their role on the blinking mechanism.

Even though fast blinking (short on time, long off time) is a limiting property in many applications, they have great potential in improving super-resolution imaging. Here, we present our preliminary FIONA (fluorescence imaging with one-nanometer accuracy) characterization using bright but fast-blinking CuInS2/ZnS quantum dots. The results show that the localization precision of CuInS2/ZnS quantum dots can reach ~1 nm, highlighting the excellent potential of these QDs for super-resolution imaging applications.

QN08.05.17

Band-Graded Light Absorber and Organic Interfacial Layer for Highly Efficient and Air-Stable PbS Quantum Dot Solar Cells

Yeong Jae Baik1 and Sohee Jeong2; 1Hankyong National University, Gyeonggi-do, Korea (the Republic of); 2Korean Institute of Machinery and Materials, Daejeon, Korea (the Republic of).

PbS quantum dot solar cell is an emerging photovoltaic technology, which is also a versatile platform in emerging memory research due to its well-developed synthesis enabling a wide range of variations in optical bandgap. Moreover, recent development in leading groups have produced power efficiency of 10%, which sheds lights in its future application areas.

In this presentation, based on the band gap engineering capability of PbS quantum dots, the development of the enhanced power conversion efficiency of band graded PbS solar cells will be presented. In addition, to further enhance the power output equipped with a good ambient stability, a systematic study on PbS quantum dot solar cells with organic hole transport layers will be presented.

Using above two elemental technologies, it is expected that the state-of-the-art technology of quantum dot solar cells would gain a further advancement.

QN08.05.18

Air Stable Nanoparticle Alloys—Synthesis and Characterization

Mary Saini Devadas1, Naveen Kadasala1, Stephen Blama2, Bryan Augustin2, Amanda Belunis1, Vera Smolyaninova2, Ellen Hondograssi1 and Maksym Zhukovskyi1; 1Department of Chemistry, Towson University, Towson, Maryland, United States; 2Department of Physics Astronomy and Geosciences, Towson University, Towson, Maryland, United States; 4Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States.

Nano-crystalline materials, because of their size, exhibit a variety of properties, which are different and often considerably improved in comparison with those of conventional polycrystalline bulk material. Of particular interest are nanoparticles of iron-cobalt because of their unique physical and chemical properties and their industrial importance in preparing magnetic recording materials, pigments, catalysts and inks. The goal of the project is to obtain alloys with the highest possible magnetization value. The metals that we have used in this study are Fe and Co. By varying the composition of the alloy nanoparticles (Fe:Co, 1:1 and 3:1) via a high temperature reduction reaction, highly stable nanoparticles have been synthesized. Their physical parameters have been characterized using TEM, XRD and composition by ICP-MS and EDX. For measuring magnetization, a home-built vibrating sample magnetometer is used. These alloys are particularly air-stable and have magnetization values that surpass the values of commercial ferrofluids, and ferrite powders. The details of the synthesis and characterization will be presented.

We acknowledge funding from NSF MRI 1626326 and DARPA AMEBA.

QN08.05.19

The Effect of Trimesic Acid Addition on the Preparation of Colloidal Sulfide Nanoparticles

José Humberto Palomares Leiva1,2; Francisco Javier Carrillo Pesquera1,3, Hilda Espanzar Ponce1, Javier Hernandez-Paredes1,3, Paul Zavala River1,2 and Ofelia Hernandez Negrete1,2; 1Universidad de Sonora, Hermosillo, Mexico; 2Departamento de Ingeniería Química y Metalurgia, Universidad de Sonora, Hermosillo, Mexico; 3Departamento de Física, Universidad de Sonora, Hermosillo, Mexico; 4Física de Materiales, Centro de Investigación en Materiales Avanzados, Chihuahua, Mexico.

There are numerous studies focused on the preparation of silica (SiO2) spheres. Most of these works have the goal to produce colloids of spherical monodisperse silica nanoparticles (NPs). However, it has been proposed that non-spherical silica NPs may have some advantages for engineering lower symmetry networks to fabricate photonic crystals. In the search for a way to prepare non-spherical silica NPs we have used different concentrations of trimesic acid (TA) during the Stöber reaction while keeping the ratio water-ethanol-TEOS-ammonia fixed. The samples were characterized by Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS) and thermal analysis (DSC-TGA). The results showed that there is an increase in the size of the silica NPs as the TA concentration increases. However, at higher concentrations of TA, not only polydispersity was
present, but also a considerable population of smaller silica spheres. There was also irregular population in the range of microns produced for disordered aggregation. Moreover, TA encourages shape anisotropy through dimer formation of silica NPs. The amount of the dimers increases with TA concentration and for the higher concentrations, aggregates of three or more silica particles were formed. These findings suggested that this route of synthesis represents an alternative method of producing anisotropic silica NPs and motivate us to continue exploring other concentrations of TA and the use of other carboxylic acid derivatives.

QN08.05.20
A Facile Synthesis of Metal-Organic Frameworks (MOFs) and MOF/Active Metal Nanoparticles Composites via Laser Ablation Synthesis in Solution Erick L. Ribeiro1, 2, 3, Barnim Khomami1, 2 and Dibyendu Mukherjee1, 4; University of Tennessee, Knoxville, Knoxville, Tennessee, United States; 2Sustainable Energy Education & Research Center (SEERC), Knoxville, Tennessee, United States; 3Nano-BioMaterials Laboratory for Energy, Energetics & Environment, Knoxville, Tennessee, United States.

The synthesis of Metal-Organic Frameworks (MOFs) has gained tremendous attention within the past decade owing to the extreme versatility of these functional materials. Although many reports on the generation of a broad variety of the MOF structures have been reported, the design of new facile, rapid and environmentally friendly fabrication strategy allowing a precise morphological and structural control of the frameworks, is still necessary. Herein, we report for the first time a methodology of laser-induced MOF formation using laser ablation synthesis in solution (LASiS) for the synthesis of zeolitic imidazolate framework-67 (ZIF-67). We have demonstrated the ability to rationally tailor the formation of the frameworks by adjusting solution-phase parameters (reagents concentration and temperature) along with laser variables (ablation time).

Secondly, we present our most recent findings in using LASiS in tandem with galvanic replacement reaction (LASiS-GRR) as a strategy and pathway for the synthesis of active metal nanoparticles (NPs) engaged in MOF structures that can exhibit unique functionalities even under extreme environments. Such encapsulation strategies can be of paramount importance in active and harsh environments where NPs need to be stabilized within the MOF structures to minimize their aggregations while conserving their properties. To this end, results for the Pt/MOF and Ag/MOF composites have shown, respectively, promising catalytic activity and plasmonic enhancement. The objective of this study is to present a complete description of the phenomena involved in this synthesis technique, allowing LASiS-GRR to be used for the fabrication of a wide range of NPs confined within MOFs crystals that go onto exhibit active catalytic, magnetic and optical properties.

QN08.05.21
A Fully Quantitative Model for Determining Growth Kinetics of Colloidal Nanoparticles Sinyu Wu and Yugang Sun; Temple University, Philadelphia, Pennsylvania, United States.

Colloidal nanoparticle synthesis has reached a level of empirical maturity with a consensus that growing well-defined colloidal nanoparticles depends on “kinetics control”. However, quantitative study of growth kinetics of colloidal nanoparticles is still missing and virtually unexplored. Rational control over growth kinetics for synthesizing colloidal nanoparticles with desirable properties on demand remains challenging. In this presentation, a strategy has been developed for analyzing growth kinetics of colloidal metal nanoparticle quantitatively by focusing both the very early and the very late growth stages, at which the size of growing nanoparticles and the reaction time follow linear functions. Applying this extreme-condition model to a microwave-assistant synthesis of colloidal silver nanoparticles, for the first time, results in the determination of intrinsic kinetics parameters involving in the growth of the silver nanoparticles. The diffusion coefficient (D) of the precursor species containing Ag+ is 4.9×10⁻¹⁴ m²/s and the surface reaction rate constant (k) of the precursor species on the surface of the growing silver nanoparticles is 8.7×10²⁵ m/s in an ethylene glycol solution containing 0.15 M polyvinylpyrrolidone at 140 °C. The extreme-condition model is ready to deconvolute the intrinsic kinetics parameters of growing colloidal nanoparticles once the enlargement rate of the nanoparticles can be experimentally measured in real time and with high temporal resolution. Availability of the high-fidelity values of k and D will provide the crucial information to guide the design and synthesis of colloidal metal nanoparticles with the desirable properties.

QN08.05.22
Milk Haptoglobin Detection Based on Enhanced Chemiluminescence of Gold Nanoparticles Giorgio Shitenberg; ARO Volcani Center, Bet Dagan, Israel.

The suggested research specifically addresses the major source of economic loss of the dairy industry, the bovine mastitis (BM), an inflammatory disease of mammary gland caused by bacterial intramammary infection. During earlier inflammation, the concentrations of acute phase proteins (APP) in both plasma and milk are escalated, which can be distinctively utilized as predicting diagnostic biomarkers of cattle’s BM clinical status. Herein, we demonstrate a liquid-phase luminol chemiluminescence (CL) system for sensitive detection of haptoglobin (Hp), a predictive APP of BM, by utilizing the binding capacity of hemoglobin (Hb). The CL intensity is linearly proportional to Hb-Hp complex formation, resulting in peroxidase-like activity inhibition of luminol-H₂O₂-Hb CL system. Enhanced CL, at least 10-fold effect within real samples, is attained by the addition of catalytically active cross-linked gold nanoparticles (GNPs) onto the luminol-H₂O₂ solution. Moreover, the influence of different somatic cell counts (representing subclinical and clinical BM status) and pathogen types (i.e., CNS and Streptococcus dysgalactiae) on the secreted milk Hp levels obtained from Holstein cows are established. The analyzed Hp concentrations are in agreement with a commercial enzyme-linked immunosorbent assay kit. The proposed CL sensing concept offers cost-effective, simple, label-free and reliable systematic analysis of Hp biomarker for BM, potentially initiating a positive effect on animals’ health and overall economy of the dairy farms.

QN08.05.23
Noble Metal/Organic Nanoparticles as a CT Contrast Agent Seong Ik Jeon and Cheol-Hee Ahn; Seoul National University, Seoul, Korea (the Republic of).

Molecular Imaging based on noble metal nanostuctures have gained interests in the field of medical applications for the past decades. Gold nanoparticles (AuNPs), also called gold colloids, are considered to be very stable and biocompatible metal nanoparticles. Previously, it was demonstrated that AuNPs modified with glycol chitosan (GC) polymers (GC-AuNPs) have excellent stability without aggregation in serum protein solution and tumor-targeting ability due to the enhanced permeability and retention effect.

Optical / PET and CT / MRI imaging are complementary visualization techniques, the former providing functional and molecular information and the latter providing anatomical details. Nanoparticles, especially metallic/inorganic nanoparticle, based imaging probes have been extensively developed to evaluate precise information about disease, utilizing their characteristic properties, such as surface plasmon resonance of gold nanoparticles and superparamagnetism of iron oxide. These characteristics provide both anatomic and functional information including the location, size and genetic details of disease by combining with NIRF imaging or PET. In spite of superb nature of these nanoparticles, they have a limitation to employ in vivo diagnosis because of their in vivo stability. Appropriate surface modification method was widely researched.

Here, we introduce several fabrication methods of nanoparticle based imaging probes and their biomedical applications. Gold nanoparticles were decorated with fluorophore labeled peptides for enzyme specific NIRF imaging and demonstrated the potential in vivo imaging probe. Gold nanoparticles, stabilized with biocompatible polymer, were prepared for in vivo NIRF/CT imaging and successfully visualized the liver and cancer. The distinguished properties of these probes showed promising potential of the activatable dual imaging probe system as a novel molecular imaging probe.

QN08.05.24
Revealing Driving Forces in Quantum Dot Supercrystal Formation Emanuele Marino1, 3, Thomas E. Kodger2, Gerard H. Wegdam1 and Peter Schall1; 1Institute of Physics, University of Amsterdam, Amsterdam, Netherlands; 2Physical Chemistry and Soft Matter, Wageningen University and Research, Wageningen, Netherlands; 3Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States.

The assembly of semiconductor nanoparticles, quantum dots (QD), into dense crystalline nanostructures holds great promise for future optoelectronic devices. However, knowledge of the sub-nanometer scale driving forces underlying the kinetic processes of nucleation, growth and final densification during QD assembly remains poor. Emulsion-templated assembly has recently been shown to provide good control over the bulk assembly of QDs by condensation into highly ordered three-dimensional supercrystals. Here, we combine emulsion-templated assembly with in situ small-angle X-ray scattering to obtain direct insight into the nanoscale interactions underlying the nucleation, growth and densification of quantum dot supercrystals. We show that at the point of supercrystal nucleation, nanoparticles undergo a hard-sphere like crystallization into a hexagonally close-
packed lattice slowly transforming into a face-centered cubic lattice. The ligands play a crucial role in balancing steric repulsion against attractive van der Waals forces to mediate the initial equilibrium assembly, but cause the QDs to be progressively destabilized upon densification. The rich detail of our kinetic study elucidates the assembly and thermodynamic properties that define QD supercrystal fabrication approaching single-crystal quality, paving the way towards their use in optoelectronic devices.

(2) Bishop, K. J.; Wilmer, C. E.; Soh, S.; Gryzowski, B. A. small 2009, 5, 1600.

SESSION QN08.06: Nanoparticle Synthesis and Applications III
Session Chairs: Hongyou Fan and Yu Han
Wednesday Morning, April 24, 2019
PCC North, 100 Level, Room 129 B

8:30 AM *QN08.06.01
Reversibly Reconfigurable Plasmonic Nanoparticle Materials David S. Ginger; University of Washington, Seattle, Washington, United States.

An exquisite sensitivity to the local environment combined with their ability to dramatically concentrate electromagnetic fields makes plasmon resonant nanoparticles ideal candidates for use in stimulus-responsive materials with potential applications ranging from biosensing to smart optics. In this talk, we explore the synthesis and characterization of reconfigurable plasmonic metallochromophores that change their structural organization, and hence their collective optical properties, in response to external stimuli such as light. We explore a variety of approaches to reversibly modulate interparticle plasmonic couplings in response to external triggers, ranging from discrete dimers functionalized with photoswitch modified DNA, to nanoparticle/polymer hybrids that enable temperature-, and photo-responsive behaviors on multiple timescales. These materials offer tunable optical responses across both the visible and near-IR. We discuss strategies for incorporating multiple stimulus-response functions, and for obtaining self-amplifying and self-limiting feedback behaviors with these materials.

9:00 AM *QN08.06.02
Autocatalytic Surface Reduction for Shape-Controlled Synthesis of Metal Nanocrystals Yousan Xia; Georgia Institute of Technology, Atlanta, Georgia, United States.

The formation of colloidal metal nanocrystals typically involves an autocatalytic process, in which the salt precursor adsorbs onto the surface of a growing nanocrystal, followed by chemical reduction to atoms for their incorporation into the nanocrystal. Despite its universal role in the synthesis of colloidal nanocrystals, it is still poorly understood and controlled in terms of kinetics. Through the use of well-defined nanocrystals as seeds, including those with different types of facets, sizes, and internal twin structure, we have quantitatively analyze the kinetics of autocatalytic surface reduction in an effort to control the evolution of nanocrystals into predictable shapes. Our kinetic measurements demonstrate that the activation energy barrier to autocatalytic surface reduction is highly dependent on both the type of facet and the presence of twin boundary, corresponding to distinctive growth patterns and products. Interestingly, the autocatalytic process is effective not only in eliminating homogeneous nucleation but also in activating and sustaining the growth of octahedral nanocrystals. This work represents a major step forward toward achieving a quantitative understanding and control of the autocatalytic process involved in the synthesis of colloidal metal nanocrystals.

9:30 AM *QN08.06.03
Impact of Surface Chemistry in Multimetallic Nanoparticle Synthesis and Performance Jill Millstone; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Metal-ligand chemistry impacts nearly every aspect of nanoparticle formation, physical properties, and utility. We develop methods to study and leverage these interactions to produce highly tailored multimetallic nanoparticles with dimensions spanning the nanoscale (1-100 nm). Here, we discuss how metal-ligand interactions may be used to mediate the incorporation and distribution of metals in and on discrete, colloidal nanoparticle substrates, as well as their optoelectronic properties once formed. In particular, we demonstrate that nanoparticle ligand chemistry may be used to access previously unobserved mixtures of metals such as continuously tunable Au-Co composition ratios, unique and Michael J. Janik

10:00 AM BREAK

10:30 AM QN08.06.04
Chromophore-Gold Superratom Clusters— Optical and Electrochemical Properties Mary Saiini Devadas1, Nicole Hondriagniess1, Angela Meola1, Brianna Hutson1, Keith Reber1 and Maxym Zhukovsky2; 1Department of Chemistry, Towson University, Towson, Maryland, United States; 2Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana, United States.

Structure and reactivity of super atom gold clusters depends on the electronic interaction between core gold atoms and the ligand. The super atom clusters of the dimension 1.1 nm containing 25 atoms of gold and 18 ligands, can be of two shapes - spherical (icosahedral); comprised of core and shell gold; made of thiol (SR) ligands; Au@4 and rod shaped (bi-icosahedral); comprised of core and bridging gold atoms; made of SR and triphenylphosphine (PPh3) ligands; Au@4-5). Both clusters are photoluminescent (PL) but Au@4-5 has higher quantum yield. In this project we push the loading of chromophores on the nanoparticle surface and compare the changes in PL as a function of geometry. Ground state electron transfer is monitored via voltammetry to investigate the direction of electron flow. The influence of the chromophore (modified coumarin and anthracene) will be investigated and quantitatively analyzed to control the evolution of nanocrystals into predictable shapes. The activation energy barrier to autocatalytic surface reduction is highly dependent on both the type of facet and the presence of twin boundary, corresponding to distinctive growth patterns and products. Interestingly, the autocatalytic process is effective not only in eliminating homogeneous nucleation but also in activating and sustaining the growth of octahedral nanocrystals. This work represents a major step forward toward achieving a quantitative understanding and control of the autocatalytic process involved in the synthesis of colloidal metal nanocrystals.

10:45 AM QN08.06.05
Doping as Strategy to Tune Color of 2D Colloidal Nanoplatelets Marion Defour1, Eva Izquierdo1, Clément Livache1,2, Bertille Martinez1,2, Thomas Pons1, Emmanuel Lhuillier2, Christophe Delerue1 and Sandrine Ihurria; 1ESPCI Paris, Paris, France; 2INS, Sorbonne Université, Paris, France; 3Université de Lille, Lille, France.

Among nanocrystals, 2D nanoplatelets appear as a special class of emitters with the best defined (ie the narrowest) photoluminescence signal. The tunability of their color is commonly obtained thanks to quantum confinement. However only discrete values for thickness can be achieved which prevent continuous tuning of the spectrum. Here we demonstrate that doping is an alternative to tune the spectrum of these II-VI semiconductor 2D nanoplatelets from green to red. We develop a synthetic method to achieve silver doping of CdSe nanoplatelets and demonstrate the potential of the material for the design of wide gamut display. Silver doing was already reported on spherical quantum dots, but several questions relative to these materials were left without firm conclusion. Here we investigate the electronic properties of the silver doped CdSe NPL using a combination of optical spectroscopy, photoemission, transport and simulation. We are finally able to build a consistent picture of the electronic level associated to the growth of octahedral nanocrystals. This work represents a major step forward toward achieving a quantitative understanding and control of the autocatalytic process involved in the synthesis of colloidal metal nanocrystals.

11:00 AM QN08.06.06
Generalized Mechanism of Foreign Metal Assisted Shape Controlled Synthesis of Silver Octahedron via Seed Mediated Growth Supriya Jharmunni1, Robert M. Rioux2, Zhifeng Chen1, Yawei Li1 and Michael J. Janik2; 1Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, United States; 2Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.
The formation of Ag octahedron nanoparticles (NPs) from Ag nanocube seeds using a foreign metal ion, Cu$^{2+}$ reported in literature has been attributed to the selective deposition of Ag on Ag(100) over Ag(111) facets, based solely upon observation of the final shape. The driving force for selective deposition of Ag on Ag(100) facets in the presence of the foreign metal ions still remains unknown. We performed a comprehensive study of the seed-mediated synthesis of Ag octahedron in presence of foreign metal ions ($M^{n+} = Ni^{2+}, Co^{2+}, Cu^{2+}, Pd^{2+},$ and Au$^{3+}$) with the objective of investigating the detailed pathway of transformation from Ag nanocube seeds to octahedron. We demonstrate a generalized mechanism based on experimental observations, periodic table trends, and theoretical calculations using density functional theory (DFT). We propose, the foreign metal ions deposit on the Ag(100) facets through either underpotential deposition (UDP) ($Cu^{+}, Ni^{2+}$ and $Co^{2+}$) or a galvanic exchange reaction (GRR) ($Pd^{2+}$ and $Au^{3+}$) depending on the $M^{n+}$ reduction potential with respect to Ag. The deposited metal induces a faster growth rate on Ag(100) facets through GRR, in the case of Cu, Ni, and Co, and through UDP in the case of Pd and Au, leading to the disappearance of Ag(100) facets and retention of Ag(111) facets. A faster growth rate on Ag(100) facets is experimentally confirmed from observation of intermediate high-index facets formed on the Ag(100) surface at higher injection rates of Ag$^{+}$. The formation of octahedron is also sensitive to the concentration of foreign metal ions added and the shape of the starting Ag seed template. This work provides a fundamental understanding of the role of foreign metal ions in seed-mediated shape-controlled synthesis of Ag octahedron, which can be extended to other more complex systems. It also offers a scope for a wide selection of foreign metal ions for shape-controlled synthesis of noble metal NPs, many of which are not explored yet, simply based on standard reduction potential values. Regardless of deposition mechanism, shape transformation from Ag(100)-bound to Ag(111)-bound structures is possible with the simultaneous addition (flux) of new Ag$^{+}$ ions.

11:15 AM QN08.06.07
Employing Colloidal Nanochemistry to Engineer Granular Magnetoresistance Materials Ben Zhou$^1$ and Jeffrey D. Rinehart$^{2, 3}$; $^1$Materials Science, University of California, San Diego, La Jolla, California, United States; $^2$Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States.

The discovery of giant magnetoresistance in 1988 enabled the explosion of hard disk drive storage capacity, and continues to impact various sensing applications today. Granular magnetoresistance, discovered shortly after giant magnetoresistance, offers similar properties in a cheaper package, but has been limited by an inability to prepare well-characterized, uniform, nanoscale magnetic domains. Employing colloidal nanochemistry to design granular magnetoresistance materials allows for explicit control of grain structure and expedient testing of different materials. We have investigated the effects of nanoparticle size on magnetoresistance and explored more complex magnetoresistive phenomena in multi-component materials.

1:30 PM QN08.07.01
In Situ Atomic-Level Tracking of Heterogeneous Nucleation in Nanocrystal Growth with an Isocyanide Molecular Probe Dong Qin and Yiren Wu; Georgia Institute of Technology, Atlanta, Georgia, United States.

We report the use of 2,6-dimethylphenyl isocyanide (2,6-DMPI) as a spectroscopic probe to study the heterogeneous nucleation and deposition of Pd on Ag nanocubes under different conditions by surface-enhanced Raman scattering (SERS). As a competitive advantage, the spectroscopic analysis can be performed in situ and in real time with the nanoparticles still suspended in the reaction solution. The success of this method relies on the distinctive stretching frequencies ($n_{NC}$) of the isocyanide group in 2,6-DMPI when it binds to Ag and Pd atoms through $\pi$ donation and $\pi$-back donation, respectively. Significantly, we discovered that $n_{NC}$ was sensitive to the arrangement of Pd adatoms on the Ag surface. For example, when the isocyanide group bound to one, two, and three Pd atoms, we would observe the atop, bridge, and hollow configurations, respectively, at different $n_{NC}$ frequencies. As such, the $n_{NC}$ band could serve as a characteristic reporter for the Pd adatoms being deposited onto different types of facets on Ag nanocubes with atomic-level sensitivity. When 2,6-DMPI molecules were introduced into the reaction solution, we further demonstrated in situ tracking of heterogeneous nucleation and early-stage deposition of Pd on Ag nanocubes by monitoring the evolution of $n_{NC}$ bands for both Ag and Pd surface atoms as a function of reaction time. This in situ technique opens up the opportunity to investigate the roles played by reaction temperature and the type of Pd(II) precursor in influencing the heterogeneous nucleation and growth of bimetallic nanocrystals. The sensitivity of isocyanide group to Pd atoms helps elucidate some of the details on the reduction, deposition, and diffusion processes involved in heterogeneous nucleation.

2:00 PM QN08.07.02
Evaporative Self-Assembly as a Powerful Tool for Creating Functional Superstructures Eugene Zubarev; Rice University, Houston, Texas, United States.

Spontaneous assembly of colloidal nanostructures is often viewed as a bottom-up alternative to lithographic techniques when it comes to creating materials with novel collective properties. The intensive research in the past 10-15 years has brought numerous examples of functional superlattices, 3D colloidal crystals, and designed patterns of nanostructures. However, the majority of self-assembly methods suffer from poor reproducibility and limited scale, which often precludes the formation of macroscopically large structures and functional devices. This presentation will focus on the evaporative self-assembly of anisotropic gold nanocrystals and the underlying mechanisms of their colloidal crystallization. In addition, template-assisted evaporative assembly of nanowires, polymers, and collagen fibers into macroscopically-large hexagonal patterns will be discussed.

2:30 PM BREAK

3:30 PM QN08.07.03
Amphiphilic Nanoparticles—Characterization and Applications Francesco Stellacci; Institute of Materials, EPFL, Lausanne, Switzerland.

In this talk the characterization of gold nanoparticles coated with an amphiphilic mixture of ligand molecules will be illustrated. In particular advances in the characterization approach via small angle neutron scattering and mass spectroscopy will be illustrated. A review of the properties will these particles will be presented. Particular attention will be devoted in illustrating the antiviral properties and the ability of these particles to effectively label amyloid fibers.

4:00 PM QN08.07.04
Mechano-Responsive Tuning of Giant Circular Dichroism in Self-Assembled Crossed Particle Chains Patrick T. Prehod$^1$, Vaibhav Gupta$^1$, Martin Mayer$^2$, Anja Maria Steiner$^1$, Günter Auenhammer$^1$, Tobias A. König$^1$, and Jeffrey D. Rinehart$^{2, 3}$; $^1$Materials Science, University of California, San Diego, La Jolla, California, United States; $^2$Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, United States; $^3$Chemistry, University of California, San Diego, La Jolla, California, United States.

Tailorable chiroptical effects in chiral plasmonic nanostructures render them promising candidates as high-efficiency broadband circular polarizers and enable enhanced direct asymmetric synthesis of chiral target molecules. Concerning flexibility in design and efficiency (circular dichroism (CD) > 10 deg), fabrication techniques like electron beam lithography and direct laser writing are usually superior to colloidal self-assembly methods (10-100 mdeg). However, using chiral templates (chiral nematic phases, DNA) or ligand-induced clustering of colloidal particles proved to be inevitable for low-cost production on large scales.

Here, we present a facile bottom-up approach to produce a crossed-chains bilayer on centimeter square area that, for the first time, is competitive ($CD = 11$ deg) to top-down methods. More interestingly, we prove significant spectral tunability (100 nm blue-shift) by mechanical deformation, which remains difficult to achieve in a post-fabrication fashion for other systems known in literature.

Two achiral nanoparticle chain arrays on compliant substrates are placed on top of each other to produce a chiral 3D arrangement of rotated chains. To this end, convective approach via small angle neutron scattering and mass spectroscopy will be illustrated. A review of the properties will these particles will be presented. Particular attention will be devoted in illustrating the antiviral properties and the ability of these particles to effectively label amyloid fibers.
Internalized Polysaccharide Nanoparticles Enhanced Production of the Natural Antimicrobial Peptide in Probiotics

Chong-Su Cho1, Whee-Soo Kim1, Liang Hong1, Sang-Kee Kang1, In-Kyu Park2 and Yun-Jiaie Choi1; 1Seoul National University, Seoul, Korea (the Republic of); 2Chonnam National University Medical School, Gwangju, Korea (the Republic of).

Antibiotics have been used in many parts of the world such as medicine, food preserving, and livestock. Abuse of antibiotics had led to an increase in inanitbiotic resistancebacterial infections in modern society. For probiotics to replace antibiotics, enhancing antimicrobial ability against pathogens is one of the key technologies on probiotics. Probiotics are not digested by human enzymes although they produce various benefictfeects to host. Polymeric nanoparticles (NPs) have been used for biomedical application because of their interesting characteristics, which enables them to overcome various biological barriers. In this study, we prepared three types of probiotics NPs usingpolysaccharides. Three type of polysaccharidessuch as inulin as a polyfructose, dextran as a polyglucoseand pullulan as a polymaltose were used. Therepriotic nanoparticles (NPs) were prepared by conjugating hydrophobic groups such as phthalylic acid, acetic anhydride, and propionic anhydride to polysaccharides. 

The anisotropic nanoparticle arrangement investigated via scanning electron microscopy (SEM) manifests in optical effects on macroscopic areas easily visible by the bare eye with the help of polarized illumination. The circular dichroism quantified by spectroscopic ellipsometry (SE) is shown to be tuned by post-fabrication change of inter-layer rotation and mechanical deformation. Possible morphological changes upon deformation are discussed to explain the reversible spectral shift, as verified by finite-difference time-domain (FDTD) simulations.

As demonstrated, simple designs cost-effectively fabricated via bottom-up techniques even stand the comparison with e-beam structures for nanoplasmonic devices. Additional tunability of the strong optical effects by external stimuli facilitates broad-band applications and opens the door for sensing applications.


4:15 PM QN08.07.05
Controlling Size, Shape and Surface Functionality of Tailored Iron Oxide Nanocrystals for Biomedical Applications

Isabel Gessner and Sanjay Mathur; University of Cologne, Cologne, Germany.

The exceptional properties of materials at the nano-scale have aroused a huge increase in their demand for a broad variety of applications. During particle engineering, precise control over physicochemical properties of the material plays a key role, allowing for a reproducible fabrication of optimized and highly efficient vectors. Although significant advances have already been made in this area, much optimization is still needed to understand the often very complex interplay between reaction parameters and obtained material characteristics.

Herein, the employment of specific surface ligands as well as controlled variation of reaction parameters during thermal decompositions, coprecipitations and solvothermal reactions enabled the synthesis of iron oxide nanoparticles (IONPs) with highly homogeneous particle morphology (spherical-, cube-, ellipsoid-shaped), size (5-200 nm) and phase (Fe3O4, Fe2O3, α-Fe2O3). The stoichiometric ratio of the precursor as well as reaction conditions also determined the formation of complex Fe3O4@Fe2O3 core-shell structures that were proven by X-ray diffraction analyses and Rieffel refinements. A subsequent functionalization with chemical linkers and biomolecules could be monitored using X-ray photoelectron spectroscopy, infrared spectroscopy as well as UV-vis spectroscopy. This step-by-step approach allowed for a very application-oriented synthesis of highly efficient MRI contrast agents as well as cancer targeting vectors.

4:30 PM QN08.07.06
Auger-Limited Carrier Recombination and Relaxation in CdSe Colloidal Quantum Wells

Matthew Pelton1, Yana Wang2, Jordan Andrews3, Igor Fedin4, Dmitri Talapin4, Haixu Long1 and Stephen K. O'Leary4; 1Physics, University of Maryland, Baltimore, Maryland, United States; 2School of Engineering, The University of British Columbia, Kelowna, British Columbia, Canada; 3Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, United States; 4Physics, University of Chicago, Chicago, Illinois, United States.

Using time-resolved photoluminescence microscopy, we show that two-exciton Auger recombination dominates carrier recombination and cooling dynamics in CdSe nanodotlest, or colloidal quantum wells. The electron−hole recombination rate depends only on the number of electron−hole pairs present in each nanodot, and is consistent with a two-exciton recombination process over a wide range of exciton densities. The carrier relaxation rate within the conduction and valence bands also depends only on the number of electron−hole pairs present, apart from an initial rapid decay, and is consistent with the cooling rate being limited by reheating due to Auger recombination processes. These Auger-limited recombination and relaxation dynamics are qualitatively different from the carrier dynamics in either colloidal quantum dots or epitaxial quantum wells. The results are determined as a function of the shell thickness. We find that the results exhibit a non-monotonic dependence on the shell thickness, initially decreasing, reaching a minimum for shells with thickness of 2–4 monolayers, and then increasing with further increases in the shell thickness.

4:45 PM QN08.07.07
Control of Ultraviolet Luminescence in Upconversion Nanoparticles

Peter Dawson, Vina Nguyen and Marek Romanowski; University of Arizona, Tucson, Arizona, United States.

Upconversion nanoparticles have matured significantly over the past decade. Preparative and post-preparative techniques have been developed to control migration, tunability, and transfer of energy. These recent advances show promise in the world of photochemical and photovoltaic systems. We demonstrate the ability to improve yield, spectrally tune, and to extinguish the UV luminescence by means of preparative controls. UV luminescence can be extinguished by means of energy migration through excess ytterbium or phonon-assisted energy transfer through secondary activator. We also demonstrate the ability to control the UV luminescence post-preparation by means of pulse-width modulation of excitation. 

Control of Ultraviolet Luminescence in Upconversion Nanoparticles

These Auger-limited recombination and relaxation dynamics are qualitatively different from the carrier dynamics in either colloidal quantum dots or epitaxial quantum wells. The results are determined as a function of the shell thickness. We find that the results exhibit a non-monotonic dependence on the shell thickness, initially decreasing, reaching a minimum for shells with thickness of 2–4 monolayers, and then increasing with further increases in the shell thickness.

SESSION QN08.08: Poster Session II: Colloidal Nanoparticle

Session Chairs: Mei Cai, Hongyou Fan, Yu Han and Han Htoon
Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

QN08.08.01
Internalized Polysaccharide Nanoparticles Enhanced Production of the Natural Antimicrobial Peptide in Probiotics

Chong-Su Cho1, Whee-Soo Kim1, Liang Hong1, Sang-Kee Kang1, In-Kyu Park2 and Yun-Jiaie Choi1; 1Seoul National University, Seoul, Korea (the Republic of); 2Chonnam National University Medical School, Gwangju, Korea (the Republic of).

Antibiotics have been used in many parts of the world such as medicine, food preserving, and livestock. Abuse of antibiotics had led to an increase in inanitbiotic resistancebacterial infections in modern society. For probiotics to replace antibiotics, enhancing antimicrobial ability against pathogens is one of the key technologies on probiotics. Probiotics are not digested by human enzymes although they produce various benefictfeects to host. Polymeric nanoparticles (NPs) have been used for biomedical application because of their interesting characteristics, which enables them to overcome various biological barriers. In this study, we prepared three types of probiotics NPs usingpolysaccharides. Three type of polysaccharidessuch as inulin as a polyfructose, dextran as a polyglucoseand pullulan as a polymaltose were used. Therepriotic nanoparticles (NPs) were prepared by conjugating hydrophobic groups such as phthalylic acid, acetic anhydride, and propionic anhydride to polysaccharides. 

The effects of phthalylinulin NPs (PINPs), phthalyldextran NPs (PDNPs), and phthalylpullulanNPs (PPNPs) on cellular and antimicrobial activities of probiotics using Pediococcus acidilactici(PA) and Lactobacillus plantarum(LP) will be mainly reported.

Firstly, PINPs were prepared by varying the molar ratio of phthalylic anhydride as a hydrophobic group to inulin, and then dialysis. We found that the internalization of PINPs into PA was size-, glucose transporter- and energy-dependent. Interestingly, PINPs-treated probiotics enhanced the production of antimicrobial peptide (pediocin) which is effective against both Gram-positive and Gram-negative pathogens. Particularly, the antimicrobial activity of PINPs-internalized probiotics was about 9-fold higher than that of untreated probiotics. Gene transcriptional analysis demonstrated the rise in pediocinactivity in PA internalized with PINPs was accompanied with the enhanced expression of genes related to
stress response and pediocinbiosynthesis genes.

To confirm the previous concept with a different type of polysaccharides, PDNPs were prepared. We observed the internalization of PDNPs into PA varied upon the transporters in probiotics and influenced higher antimicrobial activities against pathogens. The mechanism of enhancing antimicrobial property of PA was same as PA internalized with PNPs. Moreover, in PDNPs, the antimicrobial activity of PA internalized with PDNPs was also proved via animal experiments. PA internalized with PDNPs was able to suppress pathogenic infections in the gut by decreasing pathogens and increasing beneficial bacterial species which are related with prebiotics. Moreover, the composition of gut microbiota altered in PA internalized with PDNPs toward other groups. Therefore, we can conclude that higher pediocinproduction may suppress the pathogenic gut infection by altering the composition of gut microbiota.

Also, we used LP to confirm whether prebiotic NPs enhance the antibacterial ability of lactic acid bacteria as a common phenomenon because the LP is also capable of producing natural anti-microbial substances, plantaricin. When PPNNPs were added into LP, the PPNNPs were internalized into LP through energy-dependent and galactose transporter mechanism. Furthermore, more plantaricin the natural anti-bacterial peptide was secreted from the PPNNPs-internalized LP which was a similar mechanism as PNPs and PDNPs.

To the best of our knowledge, this is the first report of the concept of prebiotic NPs using polysaccharides to improve the antimicrobial activity of probiotics against pathogens. The results suggest that prebiotic NPs are new type of intracellular stimulator of probiotics to produce antimicrobial peptides, and can be used as a potential treatment of many gut disease associated with pathogens.

QN08.08.02 Oscillatory Plasmonic-Excitonic Nanomaterials Matthew S. Kirschner1, Wendu Ding1, Yuxiu Li2, Xiao-Min Lin3, Lin Chen1,3, George Schatz1 and Richard D. Schaller1,2; Northwestern University, Evanston, Illinois, United States; 3College of Chemistry and Molecular Sciences, Wuhan University of Technology, Wuhan, China; 4Argonne National Laboratory, Lemont, Illinois, United States.

We have designed nanomaterials that utilize vibrational modes to manipulate electronic interactions. Gold bipyramids with systematically varied localized surface plasmon resonance energies were functionalized with a J-aggregated thiacarbocyanine dye molecule. The resulting systems exhibit two hybridized states with clear anticrossing behavior that have a Rabi splitting energy of 120 meV. Gold bipyramids respond to photoexcitation with the generation of coherent acoustic phonons that cause oscillations in the plasmon resonance energy. In the coupled system, these photoinduced oscillations alter the metal nanoparticle’s energetic contribution to the hybridized system and, as a result, change the plasmon-exciton coupling. These modulations in the hybridization are present across a wide range of bipyramid ensembles. We discuss new analysis methods we have developed to better model this complex behavior. Such oscillatory plasmonic-excitonic nanomaterials offer a route to manipulate and dynamically tune the interactions of plasmonic/excitonic systems and unlock a range of potential applications.

QN08.08.03 Monodisperse, Phase-Pure MgFe2O4 Nanoparticles in Aqueous and Nonaqueous Media and Their Photocatalytic Behavior Roland Marshall; University of Bayreuth, Bayreuth, Germany.

We have developed a straightforward and fast non-aqueous microwave synthesis protocol using acetylacetone and acetate precursors to produce nanocrystals of the earth-abundant cubic spinel ferrite MgFe2O4[1], which is a promising material for both photoelectrochemical and photocatalytic water splitting under visible light irradiation due to its narrow band gap (~2.0 eV) and matching band positions. Highly-crystalline single phase nanoparticles with specific surface areas of around 200 m²/g and good colloidal stability in non-polar solvents were achieved, and the crystallite size can be tailored by postsynthetic heat treatment. Colloidal stabilization of the nanocrystals in nonaqueous media was realized either in-situ during synthesis or postsynthetically by surface capping with oleylamine and oleic acid. Phase transfer to aqueous media was performed employing citric acid and betaine hydrochloride, resulting in agglomerate-free and stable dispersions of citrate- and betaine-functionalized MgFe2O4 nanocrystals. Furthermore, a one-step synthesis of highly stable, water-dispersible colloids of MgFe2O4 was achieved using polyvinylpyrrolidone as stabilizer. Photocatalytic reactions will be presented evaluating the use of such highly stable ferrite colloids for solar energy conversion.


QN08.08.04 Rapid Detection of Inorganic Arsenic—A Real-Time Screening Method Based on De-Aggregation of Gold Nanoparticles Mike Bismuth1 and Giorgi Shitenberg2; 1Nanotechnology, Bar Ilan University, Ramat Gan, Israel; 2Agricultural Engineering, Volcani Center, Rishon Lezion, Israel.

The proposed research is designed as a response to the important challenge of monitoring inorganic arsenic (iAs+3) pollutants in the environment. Arsenic is one of the most serious environmental pollution problems of our time, specifically in developing countries, owing to its widespread in nature and high toxicity to living organisms. Long-term exposure causes serious physiological implications i.e., heart disease, stillbirth and cancer, requiring frequent determination in water, soil, agricultural and food samples. Traditional methods of detection, together with the advanced rapid techniques, possess major on-site limitation revealing their inadequacy for real-time analysis. Thus, an early and rapid detection of iAs+3 followed by corrective and/or prevention actions can lead to reduction of overall polluting impact to safeguard public health. The main goal of this project is to develop a generic integrated biosensing platform for the detection and quantification of iAs+3 pollutants in aqueous solutions at low-level concentrations. Gold nanoparticles (GNPs) play a key role in the development of smart sensors and detection agents. Their high surface to volume ratio and unique optical properties facilitate the development of highly sensitive analytical tools for biosensing applications accompanied with the advantages of on-site applicability. Addition of real water to the GNPs induces aggregation, attributed to the water’s high salinity content by screening the negative charges that stabilize them. Herein, our sensing approach is based on nanoparticles de-aggregation mechanism. Furthermore, more plantaricin the natural anti-bacterial peptide was secreted from the PPNNPs-internalized LP which was a similar mechanism as PNPs and PDNPs.

QN08.08.05 Cost Effective Bandgap Tunability Through Ordered Doped Zinc Oxide Nanostructure Films Clinton Davis and Hemali Rathnayake; Nanoscience, University of North Carolina at Greensboro, Greensboro, North Carolina, United States.

Zinc oxide (ZnO) has gained popularity over the years for being an inexpensive semiconductor while having a wide bandgap of 3.37 eV, making it a possible candidate for replacing other materials that have a higher cost. Furthermore, by adding dopant materials and/or nanostructures the bandgap can be precisely tuned for specific applications. While other doping options exist, cation exchange gives the advantage that the structure is already formed and is simply adding an extra step to the synthesis process. The doped-ZnO structures were analyzed with SEM and TEM to confirm homogeneity and the presence of the dopant material. The results show that through facile synthesis via cation exchange, shifts in the bandgap up to 0.1 eV were achieved consistently in dilute concentrations ranging from 1-5%. XRD was used to confirm the dopants were part of the crystalline lattice by the shift of the wurtzite peaks.

QN08.08.06 Matrix-Free Stabilization of DNA-Engineered Colloidal Crystals with Silver Ions Taegon Oh, Sarah S. Park and Chad A. Mirkin; Northwestern University, Evanston, Illinois, United States.

A post-synthetic method for stabilizing colloidal crystals programmed from DNA has been developed. The method relies on Ag+ ions to stabilize the particle-connecting DNA duplexes within the crystal lattice, essentially transforming them from loosely bound structures to ones with very strong interparticle links. Such crystals do not dissociate as a function of temperature like normal DNA or DNA-interconnected superlattices, and they can be moved from water to organic media or the solid state, and stay intact. The Ag+-stabilization of the DNA bonds is accompanied by a nondestructive ~25% contraction of the lattice, and both the stabilization and contraction are reversible with the chemical extraction of the Ag+ ions, by AgCl precipitation with NaCl. This synthetic tool is important, since it allows scientists and engineers to study such crystals in environments that are incompatible with structures made by conventional DNA programmable methods and without the influence of a matrix such as silica.
Control Over Colloidal Supercrystal Formation with Density Layers

Taegon Oh\textsuperscript{1}, Jessie C. Ku\textsuperscript{1}, Jae-Hyeok Lee\textsuperscript{2}, Mark C. Hersam\textsuperscript{3} and Chad A. Mirkin\textsuperscript{1}; \textsuperscript{1}Northwestern University, Evanston, Illinois, United States; \textsuperscript{2}Korea Institute of Toxicology, Daejeon, Korea (the Republic of).

With the advent of DNA-directed methods to form “single crystal” nanoparticle superlattices, new opportunities for studying the properties of such structures across many length scales now exist. These structure-property relationships rely on the ability of one to deliberately use DNA to control crystal symmetry, lattice parameter, and microscale crystal habit. Although DNA-programmed colloidal crystals consistently form thermodynamically favored crystal habits with a well-defined symmetry and lattice parameter based upon well-established design rules, the sizes of such crystals often vary substantially. For many applications, especially those pertaining to optics, each crystal can represent a single device, and therefore size variability can significantly reduce their scope of use. Consequently, we developed a new method based upon the density difference between two layers of solvents to control nanoparticle superlattice formation and growth. In a top aqueous layer, the assembling particles form a less viscous and less dense state, while below the particles assemble into well-defined rhombic dodecahedra superlattices of a critical size, they sediment into a higher density and higher viscosity sublayer that does not contain particles (aqueous polysaccharide), thereby arresting growth. As a proof-of-concept, this method was used to prepare a uniform batch of Au nanoparticle (20.0 ± 1.6 nm in diameter) superlattices in the form of 0.95 ± 0.20 µm edge length rhombic dodecahedra with body-centered cubic crystal symmetries and a 49 nm lattice parameter (cf. 1.04 ± 0.38 µm without the sublayer). This approach to controlling and arresting superlattice growth yields structures with a three-fold enhancement in the polydispersity index.

Synthesis and Characterization of the Solid Solution of Bismuth Sulfate, Potassium Bismuth Titanate and Barium Titanate (bnkt-bt) Perovskite Type

Emmanuel M. Rodriguez, Hector C. Montes and Gamaliel H. Cuevas; Universidad Autonoma de Ciudad Juarez, Juarez, Mexico.

The ceramic compound 0.94(0.8Bi\textsubscript{2}O\textsubscript{2}S\textsubscript{3} - 0.2Bi\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}) - 0.06(BaTiO\textsubscript{3}), a lead-free piezoelectric perovskite type, was obtained by the sol-gel synthesis method in search for the single phase solid solution. Different starting combinations for this ceramic were used: i) nitrates as precursors (BNKT-BT), ii) bismuth acetate (BNKT-BT/BAc), iii) barium acetate (BNKT-BT/BAc) exposed to a shock gelation (SG) and iv) barium acetate with extensive gelation (EG). Once the solid solution was attained, a pressure less sintering (PLS) process at different temperatures (1000 °C, 1050°C, 1100°C) was performed. Samples were analyzed by X-ray diffraction and Raman spectroscopy to elucidate the grain morphology and crystallographic structure. Dielectric properties were measured using impedance and capacitance spectroscopy. Results are presented and discussed.

Next Generation Liquid-Crystal-Display Using Eco-Friendly InP Based Quantum-Dot Functional Color-Filters Ultra High Resolution LCD

Seung-Jae Lee, Ji-Eun Lee, Seo-Yoon Kim and Jea-Gun Park; Han-Yang University, Seoul, Korea (the Republic of).

Recently, the quantum-dot enhancement film (QDEF) has been introduced to improve the color gamut for LCD technology. Although this QDEF has been realized approximately zero cross-talk among the main three RGB colors, it leads to the loss of the light power of back light unit due to the resin and barrier sheets. Therefore, we introduce a simple and cost-effect structure for conventional blue LED back light unit (BLU) LCD having no QDEF but higher resolution and wider color gamut by mixing InP-QDs directly into the color filter. This structure is called quantum-dot-color-functional-QDCF.

To apply this proposed structure of QD-functional CFs to an ultra-high resolution LCD application, the color gamut performance of the LCD-like micro-displays using blue, green, and red CFs were estimated by using the CIE 1931 color space with Rec. 2020 and NTSC 1953 standards. Then it compared with that of the conventional LCD like micro displays using the white LED BLU and conventional CFs. The CIE coordinates of three types of micro-displays using green and red InP-QD color filters were calculated by using the PL spectrum information and the Matlab-based CIE coordinate calculator software. It was confirmed that green and red InP-QD emit a light at the wavelengths of 530, and 632 nm having narrow PL-FWHM of 39, 47 nm and high PL-QY of about 85, 55 %, respectively. The RGB color gamut of the conventional LCD-like micro-displays using bLED BLU and conventional CFs showed only 73.7 % (NTSC) and 55.1 % (Rec. 2020). On the other hand, the RGB color gamut of the proposed LCD-like micro-displays using the fabricated InP-QD function CFs presented a higher value of (NTSC) and 81.4 % (Rec. 2020) due to the zero cross-talk among PL spectrums of RGB colors. We will present in detail the RGB color gamut of InP-QD color filters in view point of optical properties of QDFs and LCD display operation.

Colloidal “Black” TiO\textsubscript{2} Nanoparticles and Mesoporous Films—Synthesis, Optical Properties, Processing and Photocatalytic Activity

Julia I. Chang\textsuperscript{1}, Tiago F. Silva\textsuperscript{2}, Fabian Naab\textsuperscript{3}, Bin Yuan\textsuperscript{4}, Xinchun Tian\textsuperscript{1}, Lin Ma\textsuperscript{5}, Soubik Banerjee\textsuperscript{1} and Ludovico Cademartiri\textsuperscript{1, 5, 6}; \textsuperscript{1}Materials Science & Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; \textsuperscript{2}Ria do Matão, Instituto de Física da Universidade de São Paulo, São Paulo, Brazil; \textsuperscript{3}Michigan Ion Beam Laboratory, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; \textsuperscript{4}Chemical & Biological Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; \textsuperscript{5}U.S. Department of Energy, Ames Laboratory, Ames, Iowa, United States.

A modified Collodin's method (I) was used to make colloidal “black” TiO\textsubscript{2} nanoparticles with high monodispersity. The absorption and luminescence of these particles were investigated. In order to study the photocatalytic performance of these nanocrystals we used them as building blocks to make, in two steps, TiO\textsubscript{2} mesoporous films by processing spincoated TiO\textsubscript{2} nanocrystal solids with plastics. Furthermore, to investigate the role of N-doping we demonstrate that plasma processing in N\textsubscript{2} plasma allows to simultaneously remove the ligands and dope homogeneously the mesoporous films with interstitial N. Lastly we will show how doping and processing affects the photocatalytic activity of the mesoporous films under both UV and visible light.

Metal-Free Phosphor Carbon Dots for Near UV Pumped White LEDs Through the Förster Resonance Energy Transfer

Dan Qiu\textsuperscript{1}, Wenhan Sun\textsuperscript{2} and Zaiqing Sun\textsuperscript{1}; \textsuperscript{1}Beijing Institute of Technology, Beijing, China; \textsuperscript{2}The Barstow School, Kansas City, Missouri, United States.

It is a critical challenge to develop a single phase phosphor with high luminous efficiency, Ra and suitable correlated color temperature (CCT). Comparing with traditional rare-earth based phosphors, carbon dots (CDs) possess various merits such as broad and tunable emission, excellent photostability and low cost and toxicity. Thus, CDs are ideal single phase phosphor materials, which emission can cover the whole visible spectrum. However, as-prepared CDs display strong blue emission with a broad tail in most cases. Towards making CDs as a single phase white-light phosphor, the emission at a longer wavelength has to be enhanced to balance the PL spectrum by increasing both the content and PL QY of long wavelength emissive CDs. On the other hand, more green and red emissive CDs can be excited by blue and green light, not UV light. Thus, it is necessary to further promote the energy transfer from blue emissive CDs to green and red emissive CDs. In this work, WCDs can be simply synthesized from the o-phenylenediamine (PDA) and the catechol in the mixture of n-amyl alcohol (NAA) and dimethylformamide (DMF) by one-step hydrothermal. The WCDs exhibits broad UV-vis light absorption band and strong excitation-dependent emission covering blue (450nm), green (520 nm) and red (600 nm) light with PL QY of 0.42, 0.55 and 0.67, respectively. We addressed that B-CDS, G-CDS,
and R-CDs were from the carbonization of pure catechol, PDA and the complexes of catechol and PDA (named as complexes CP). With the increase of the concentration of WCDs, the B- and G-CDs tend to form J-aggregates, R-CDs can organize in both H- and J- aggregate ways. The aggregates make thePLE spectrum shift, which leads to that the B- and G-CDs can be directly excited by UV light. Although R-CDs cannot be directly excited by UV light, it can emit red light via FRET route due to they have a spectral overlap between donor and acceptor. Finally, WLEDs device is constructed and demonstrate that WCDs can be used as the phosphor for white lighting due to its high CRI of 93, low CCT of 5453 K and high luminous efficiency.

QN08.08.13
Synthesis, Characterization and Thermoluminescence Response of Graphitic Carbon Nitride Quantum Dots Mario C. Perez, Miguel Vallejo, Cristian Gomez, Pablo V. Ceron, Jesus Bernal and Modesto A. Sosa; Univ de Guanajuato, Leon, Mexico.

Quantum dots (QD) are very small semiconductor particles, only several nanometers in size, so small that their optical and electronic properties differ from those of larger particles. Many types of quantum dot will emit light of specific frequencies if electricity or light is applied to them, and these frequencies can be precisely tuned by changing the dots’size, shape and material, giving rise to many applications. In the present work we present the synthesis for the obtaining of quantum dots from the Graphitic Carbon Nitride(g C3N4), this is a family of carbon nitride compounds with a general formula near to C3N4 (albeit typically with non-zero amounts of Hydrogen). Graphitic carbon nitride can be prepared by a heat treatment of the Urea, also known as carbamide. Urea is an organic compound with chemical formula CO(NH2)2 and have an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. It is a colorless, odorless solid, highly soluble in water, and practically non-toxic. We prepared the quantum dots with a Hydrothermal synthesis: can be defined as a method of synthesis of single crystals that depends on the solubility of materials in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave. A morphological characterization was made with X-ray diffraction and SEM(Scanning Electron Microscopy) to our material (g C3N4), to reveal information about the crystal structure and chemical composition, before during and after the process. We also investigated the photoluminescence properties of g C3N4 quantum dots, which when excited with a wavelength λ = 366 nm we obtain a blue emission, also we made a UV-Vis characterization in order to observe the absorption band of the carbon nitride. The thermoluminescent response is also reported of this quantum dots in order to use it as an application in clinical dosimetry.

QN08.08.14
Fabrication of Porphyrin Assemblies and Biological Applications Jinhuan Wang and Yong Zhong; Key Laboratory for Special Functional Materials of the Ministry of Education, Kaifeng, China.

Porphyrins play a very important role in life activities and are known as "living dyes". Porphyrin molecules have high molar extinction coefficient, good bio-source, certain photostability and thermal stability, which have wide application in biological diagnosis and treatment. Porphyrin assemblies obtained by surfactant-assist self-assembly strategy drive non-covalent interaction offsetting the narrow absorption of monomer and improving the dispersity of water. Our research group are dedicated to the research of porphyrin assemblies in biotherapeutics and have achieved some exciting results. We used zinc meso-tetra(4-pyridyl)porphyrin (ZnTPyP) as activity function building block, ZnTPyP@(SiO2) composite structure was conducted through a combined surfactant micelle confined self-assembly and silicate sol–gel process with good biocompatibility and high single oxygen yield, and the apoptosis rate reached 90% after folic acid modification. In addition, Nitric oxide (NO) coordinates to central metal Zn ions of ZnTPyP nanoparticles and formed stabilized ZnTPyP@NO nanoparticles. We show that ZnTPyP@NO photosensitizers release highly reactive peroxynitrite molecules under light irradiation and exhibit enhanced antibacterial photodynamic therapy (APDT) activity. Recently, we have used 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) as optical active precursor, and the absorption spectrum of TAPP nanoparticles obtained by protonic acid-mediated assembly can broaden to about 1000 nm. The TAPP assemblies exhibit excellent morphology dependent NIR photothermal properties and effects. These consequences provide an important reference for the application of porphyrin self-assemblies in biological therapy.

QN08.08.15
Surface-Engineered Carbon Quantum Dots for High Quantum Yields and Their Photonic Applications Heetae Ahn, TaeGuen Kim and Na Young Ha; Ajou University, Suwon, Korea (the Republic of).

Fluorescent carbon quantum dots (CQDs) have been attractive from chemical inertness, facile modification, high water-solubility, low photo-bleaching, and excellent biocompatibility [1]. Here, to obtain surface-engineered CQDs with high photoluminescence (PL) quantum yield (QY), we employed a one-step microwave synthesis route based on citric acid and cyaniste. For various CQDs synthesized under different cysteine ratios, physical and chemical properties of CQDs were investigated by using the transmission electron microscope (TEM), the Raman, and the X-ray photoelectron spectroscopy (XPS) systems. From the TEM images, CQDs were spherical nanoparticles with the size in the range of 2 - 4 nm and the average lattice spacing of C-dots was 0.21 nm. The Raman spectra showed contributions from both the G-band (in-plane vibration of sp2 carbon) and the D-band (the presence of sp3 defects). In the XPS spectra, we found that the surface amino group of the CQDs increased with increasing the cysteine ratio. These surface-engineered CQDs sample with high density of surface amino groups exhibit high PL QY of ~76 %.

Glucose, used in this study is a kind of sugar and an important biological raw material that can be easily extracted in nature without any purification [2]. We fabricated glucose films doped with CQDs by spin-coating of the aqueous solution of CQDs and glucose. We also introduced a periodic nanostructure on the CQD film by using a nanoimprint lithography process [3]. The nanostructured CQD films showed strong enhancement of photoluminescence efficiencies at the specific spectral region depending on the periodicity of the nanostructured films. These nanostructured CQD films can be new light sources and photonic devices for health care.


QN08.08.16
Characterization and Analysis of Photocatalytic Performance of Potassium-Doped Titanium Oxide Nanostructures Prepared via Wet Corrosion of Titanium Microspheres So Yoon Lee1, Ji Zhang1, Lee-Woon Jang1, Zhihong Zhang1, Yueji Guo1, Samir Salameh1, Sanghoon Kim2, Dong Ick Son2, Jean-Pierre Locquet3 and Jin Won seo4; 1Institut für Werkstofftechnik, Universität Bremen, Bremen, Germany; 2Department of Physics, University Of Ulsan, Ulsan, Korea (the Republic of); 3Soft Innovative Materials Research Center, Korea Institute of Science and Technology, Wanju, Korea (the Republic of); 4Department of Materials Engineering, KU Leuven, Leuven, Belgium; 5Department of Physics and Astronomy, KU Leuven, Leuven, Belgium.

To date, Ti-based nanostructures have attracted a considerable amount of attention in photocatalysis, photovoltaics, electrochemical devices, electrochemistry, biointerfaces and corrosion because of their unique and diverse physico-chemical properties. Among them, potassium (K) incorporated Ti-based nanostructured oxides (KTOx) have received particular attention due to their wide range of applications as previously mentioned and because of their remarkable structure. KTOx materials are versatile, and through control of the K content, the electrical and optical properties can be fine-tuned. Moreover, whereas other metal oxide particles for photocatalysis such as CdS or GaP degrade and produce toxic end-products, the catalytic activity of KTOx only involves photosynthesis without additional chemicals, resulting in an environmentally friendly product. One of the main bottlenecks in using KTOx for diverse applications is the nanostructures fabrication, which generally involves a complicated process with low reproducibility and high cost of chemical modifications. The physical properties of KTOx, which are made by chemical modification greatly affected by the incorporated K in the obtained KTOx, thereby reducing the various the size and morphology of the nanostructures. On the basis of this result, the precious amount of the incorporated K is a key issue to control the desirable properties. Herein, the development of a process that allows simple synthesis and tuning of the desired morphology and properties is currently an important roadblock in this research field.

In this contribution, KTOx nanowires were prepared by wet corrosion process (WCP) and had their photocatalytic effects systematically characterized. In the synthesis of the KTOx, the potassium hydroxide (KOH) concentrations were varied during the WCP in order to obtain nanostructures with different surface areas and surface charges. Structural and crystalline properties of the KTOx were studied by means of X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Chemical composition was determined through X-ray fluorescence and energy-dispersive X-ray analysis. Photocatalytic performance was investigated as a function of the surface area, pH, and crystalline structures by studying the degradation of methylene blue, cardiogreen, and azorubine red dyes upon UV irradiation. Note that the heat treatment was carried out to increase the crystallinity of KTOx. The results demonstrated that the negatively charged crystalline KTOx nanostructures with high surface area showed significantly higher photocatalytic degradation when compared to KTOx with low crystallinity. The produced KTOx also showed greater efficiency for recovery and re-use. The heat treatment
Institute of Science and Technology, Barcelona, Spain. Optical Gain Modulation of a Colloidal Quantum Dot Film in an Electrical Device. EBSD, in-column BSD detectors, and STEM) are studied. In addition parameters for EDX mapping will also be presented, especially for elemental analysis of alloys. Details of the with spin coating followed by plasma cleaning, with controlled plasma composition. System parameters of spot size and accelerating voltage for different built-in detectors (ETD, EBSD, in-column BSD detectors, and STEM) are studied. In addition parameters for EDX mapping will also be presented, especially for elemental analysis of alloys. Details of the.

Colloidal sulfide nanocrystals have shown potential applications in a variety of fields, such as solar cells, biological labeling and imaging, catalysis, sensors etc. Currently, the translation of these nanocrystals to industrial products is greatly hampered by their lack of sustainability (e.g. low energy efficiency, copious waste, low yield etc.), scalability (e.g. one gram per batch), and high cost of synthesis. As previously identified by other members of the community, the high cost of production is the key bottleneck in the use of sulfide nanocrystals in solar cells.

We will show how a novel renewable liquid sulfur precursor, oleylammonium hydrosulfide, allows for a drastic improvement in the sustainability, scalability, and cost profile of the synthesis of a number of sulfide compositions (PbS, Bi$_2$Se$_3$, Ag$_2$S, Cu$_2$S, etc.). Specifically, this precursor allows for (i) the synthesis of monodisperse nanocrystals under ambient condition (rather than at high temperatures and inert conditions), (ii) facile recycling of excess precursor, (iii) high reaction yield (> 70%) at short reaction times, (iv) high product concentration (90 g L$^{-1}$), and facile scalability to > 100 g per batch.

**QN08.08.17**

**Sustainable and Low-Cost Synthesis of Sulfide Nanocrystals by an Ionic Liquid Precursor** Bin Yuan$^1$ and Ludovico Cademartiri$^{1,2,3}$; $^1$Chemical & Biological Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; $^2$Materials Science & Engineering, Iowa State University of Science and Technology, Ames, Iowa, United States; $^3$Ames Laboratory, Ames, Iowa, United States.

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**QN08.08.18**

**Numerical Modeling of Growth of Faceted Gold Nanoparticles by Chemical Salt Reduction Method** Guan-Ping Jhao and Kun-Dar Li; National University of Tainan, Tainan, Taiwan.

Over the past decades, gold nanoparticles have been extensively studied in many scientific and technological fields from organic photovoltaics, electronic conductors and catalysis, because of their unique optoelectronic properties. The optical and electronic properties of gold nanoparticles are tunable by changing the shape, size, surface chemistry, or aggregate state. In this research, a theoretical model based on the phase-field approach is established to simulate the growth of hexahedron gold nanoparticles by chemical salt reduction method. The nucleation, growth and clustering processes of gold nanoparticles are rebuilt in the numerical calculations. By tuning the numerical parameters, such as the concentration of solution, temperature, and the crystalline orientation, in the simulations, the effects of the relevant experimental parameters on the formation and evolution of faceted gold nanocrystals can be realized. From the numerical simulation results, it demonstrated that the morphologies of the nanocrystals were significantly affected by the anisotropic strength of the crystals, while the size or the aggregation rate of the nanoparticles were varied with the diffusion conditions of ions in the solution. These numerical parameters can be connected to the experimental factors, e.g. the pH or temperature. This numerical study could be useful to improve the understanding of the formation and evolution of faceted gold nanoparticles by chemical salt reduction method.

**QN08.08.19**

**Imaging Magnetic and Non-Magnetic Nanostructures Using a Field Emission Scanning Electron Microscope Including STEM Mode** Mary Saiini Devadas$^1$ and Stephen Blamé$^2$; $^1$Department of Chemistry, Towson University, Towson, Maryland, United States; $^2$Department of Physics Astronomy and Geosciences, Towson University, Towson, Maryland, United States.

An electron microscope can be used to image materials of nanoscale dimensions allowing for examination of size and shape characteristics, and chemical composition. We use an FEI Apreo scanning electron microscope to image magnetic (using electromagnetic mode) and nonmagnetic nanostructures (using electrostatic mode) of various metals (Au and Ag) and metal alloys (Fe/Cu, Fe/Au) using different sample preparation methods, and varying system parameters for optimal image quality and resolution. Samples are prepared with spin coating followed by plasma cleaning, with controlled plasma composition. System parameters of spot size and accelerating voltage for different built-in detectors (ETD, EBSD, in-column BSD detectors, and STEM) are studied. In addition parameters for EDX mapping will also be presented, especially for elemental analysis of alloys. Details of the imaging parameters and sample preparation for SEM imaging will be presented. We acknowledge funding from NSF MRI 1626326.

**QN08.08.20**

**Optical Gain Modulation of a Colloidal Quantum Dot Film in an Electrical Device** Jinhue Yu, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Songyan Hou, Chathuranga Hettiarachchi, Savas Delikanli, Pedro Hernández-Martínez, Muhammad D. Birowsouto, Hong Wang, Hilmi V. Demir and Cuong Dang; Nanyang Technological University, Singapore, Singapore.

In view of optical gain application, colloidal quantum dots (CQDs) are suffering from band-edge state degeneracy which requires multiple-exciton to achieve population inversion. However, fast and efficient Auger process in the CQDs containing multiple-exciton increases the lasing threshold and limits the gain lifetime. Here, by applying the electric field to the quasi-type II CQDs (CdSe/CdS/ZnS core/shell/shell) embedded in the Sawyer–Tower circuit, we have demonstrated tunable amplified spontaneous emission (ASE) threshold in a long-sought practical device where the CQDs sandwiched between two dielectric layers retain their high quantum efficiency as in parent solution (quantum yield of > 70%). Singly-charged CQDs help building up population inversion due to pre-existing electrons while strongly enhanced Auger recombination in multiple-charged CQDs (i.e., doubly charged exciton) stifmes the optical amplification. This approach allows us to fine-tune and achieve the optimal charging level to utilize the advantages of singly charged CQDs and reduce the adverse effect of doubly charged CQDs.

In addition to demonstrating tunable optical gain experimentally, we also developed a kinetic equation model to systematically analyze the electric field dependent light amplification behavior theoretically. The kinetic model not only confirms our experimental results but also presents to be a reliable tool for accessing the requirements of the charging level to achieve nearly zero-threshold gain in CQDs. The implications, then, to potential applications of our robust and environment-undependable tuning method are broad, from controlling exciton recombination dynamics to continuous wave (CW) or possibly electrically pumped CQD lasers.

**QN08.08.21**

**Doped Lanthanum Hafnate Pyrochlore Nanoparticles as Promising Candidate of Multicolor NUV Phosphors for Warm White Lighting** Santosh Gupta, Jose Zuniga, Maya Abdou and Yuanming Mao; The University of Texas at Rio Grande Valley, Edinburg, Texas, United States.

Designing nanoparticles (NPs) for multifunctional applications towards phosphors, scintillators and white light emitting diodes is highly challenging and demanding. In this work, we explored pyrochlore La$_2$Hf$_2$O$_7$ NPs singly and triply doped with Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$. The NPs singly doped with Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$ displayed red, green and yellow/orange-blue emission under ultraviolet irradiation, respectively. The concentration quenching study revealed non-radiative energy transfer in Eu$^{3+}$ doped La$_2$Hf$_2$O$_7$ NPs takes place via dipole-quadrupole mechanism whereas dipole-dipole interaction prevails in Tb$^{3+}$ and Dy$^{3+}$ doped La$_2$Hf$_2$O$_7$ NPs. Furthermore, when triply doped with Eu$^{3+}$, Tb$^{3+}$ and Dy$^{3+}$ ions, the La$_2$Hf$_2$O$_7$ NPs display beautiful warm white light as a new strategy with color tunability through doping percentage. Lifetime spectroscopy reveals the stabilization of Eu$^{3+}$ and Dy$^{3+}$ ions at La$^{3+}$ site at low doping concentration whereas a fraction of them migrates to Hf$^{4+}$ site at high doping concentration. For the La$_2$Hf$_2$O$_7$: Tb$^{3+}$ NPs, Tb$^{3+}$ ions are localized at Hf$^{4+}$ site at all doping concentrations. To sum, our complete spectrum of studies on the structure, UV excited photoluminescence, concentration quenching, local site spectroscopy of the La$_2$Hf$_2$O$_7$ NPs suggests that they are potential candidates as single-component multicolor-emitting phosphors.

**QN08.08.22**

**Cadmium Chloride Induced Synthesis of CdSe Nanoplatelets with Increased Thickness** Sotirios Christodoulou$^{1,4}$, Juan Climente$^1$, Josep Planellés$^2$, Rosaria Brescia$^1$, Mirko Prato$^1$, Beatriz Martín-García$^1$, Ali Hossain Khan$^{3,4}$ and Iwan Morel$^{1,2}$; $^1$Nanotechnology, Istituto Italiano di Tecnologia, Genova, Italy; $^2$Chemistry Department, Ghent University, Ghent, Belgium; $^3$Departament de Química Física i Analítica, Universitat Jaume I, Castelló de la Plana, Spain; $^4$IICFO - Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, Barcelona, Spain.

Two dimensional (2D) semiconductor nanoplatelets (NPLs) have received significant attention because of their unique narrow emission spectra and fast fluorescence
lifetimes.\textsuperscript{(1)} NPLs exhibit strong quantum confinement only along the vertical direction, which can be controlled with atomic precision.\textsuperscript{(1)} So far, blue (460 nm) and green (510, 550 nm) emitting colloidal CdSe NPLs have been intensely investigated,\textsuperscript{(1)} however one also requires thicker nanoplatelets, to cover the remaining visible spectrum and for instance obtain narrowband red emitters.

Here we present a novel synthetic approach to obtain thicker CdSe NPLs. The introduction of small amounts of CdCl\textsubscript{2} switches the 2D growth of 4.5 monolayer (ML) NPLs to a more isotropic 3D growth, resulting in a series of nearly monodisperse CdSe NPLs with thicknesses from 5.5 ML to 8.5 ML.\textsuperscript{(2)} The thickness tuning has been achieved by varying the reaction temperature between 280-320°C. The growth mechanism was studied by monitoring the reaction kinetics and control experiments of purified NPL dispersions, which suggest that the thickness increases via Ostwald ripening.\textsuperscript{(2,3)}

Structural characterization by X-ray diffraction and transmission electron microscopy revealed that the NPLs maintain a zinc-blende crystal structure, despite growing them for 2-5 hours at high temperatures. Optical characterization yielded emission peaks at 534, 585, 605 and 625 nm for thicknesses from 5.5 ML up to 8.5 ML, respectively. They show fast emission lifetimes of 5-11 ns and maintain narrow emission line widths of 9-13 nm (FWHM), making them one of the narrowest colloidal nanocrystal emitters currently available in this spectral range. Photoluminescence excitation spectra of the thicker NPLs revealed several high-energy peaks, which has been assigned using k.p calculations.

To summarize, we have successfully synthesized CdSe NPLs with increasing thickness by introduction of chloride ions in the synthesis. This has enabled us to obtain narrow, fast emitters over a wide spectral range, and yielded additional insights into both the synthesis mechanism as well as the NPL optoelectronic properties.

Acknowledgement: This project has received funding from the European Research Council (Grant no. 714876 PHOCONA).

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QN08.08.23

The Development of Novel Multimodal Magnetic Plasmonic Nanocomposites for Applications in Biosensing and Thermotheranostics
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The combination of magnetic and plasmonic functionalities into one nanocomposite material is the basis of many new multifunctional nanomaterials with unique multimodal properties. Such materials retain all functionality of the magnetic component (e.g. for use in magnetic separation, as MRI contrast agents etc.), but with the added functionality of a plasmonic component (e.g. for use in SERS). The majority of magnetic-plasmonic nanomaterials are core-shell in structure, and this results in a number of inherent difficulties. Direct coating of a plasmonic metal onto a magnetic ferrite is difficult due to a mismatch in their crystal lattices. This result is achieved through a simple, highly reproducible co-precipitation method which can easily be extended to other magnetic ferrites and plasmonic metals.

In this work, a novel approach to magnetic-plasmonic nanocomposites has been developed through utilisation of two non-toxic and biocompatible polyelectrolytes, polystyrene-sodium sulfonate (PSS) and poly(allylamine hydrochloride) (PAH). Negatively charged PSS was used to stabilise superparamagnetic Fe\textsubscript{3}O\textsubscript{4} nanoparticles, while positively charged PAH was used to stabilise gold nanoparticles. The subsequent combination of these two moieties resulted in the formation of a magnetic-plasmonic nanocomposite that is bound entirely through electrostatics. This result is achieved through a simple, highly reproducible co-precipitation method which can easily be extended to other magnetic ferrites and plasmonic metals.

This approach was then extended to a number of systems, including gold nanostars with magnetite vesicles, multilayer magnetic plasmonic microspheres and magnetite coated plasmonic nanowires. We plan to explore the applications of these new nanomaterials in magnetic separation and sensing, as well as their potential applications in new drug delivery systems and in diagnostics and therapy (e.g. hyperthermia).


QN08.08.24

Identification and Semi-Quantification of Porphyrin-Silica Composite Nanoparticles Using Atmospheric Solids Analysis Probe Mass Spectrometry
Dongmei Ye, Casey Karler, Kylea Parchert, James Ricken, Bryan Carson, Curtis Mowry and Hongyou Fan; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Porphyrins are vital pigments involved in biological energy transduction processes. Their abilities to absorb light, then convert it to energy, have raised the interest of using porphyrin nanoparticles as photo-sensors in photodynamic therapy processes. A recent study showed that self-assembled porphyrin-silica composite nanoparticles can selectively destroy tumor cells, but detection of the cellular uptake of porphyrin-silica composite nanoparticles was limited to imaging microscopy. Here we developed a novel method to rapidly identify and semi-quantify porphyrin-silica composite nanoparticles using Atmospheric Solids Analysis Probe-Mass Spectrometry (ASAP-MS). ASAP-MS can directly analyze composite nanoparticles were released. Vaporized nanoparticles were ionized and detected by MS. The cellular uptake of porphyrin-silica composite nanoparticles was identified to remove residual nanoparticles, the cell suspension was loaded onto the end of ASAP glass capillary probe. Upon heating, HeLa cells were degraded and porphyrin-silica composite nanoparticles were released. Vaporized nanoparticles were ionized and detected by MS. The cellular uptake of porphyrin-silica composite nanoparticles was identified using this ASAP-MS method, and their cellular accumulation was quantified. Thus, this study established a quantification toolkit for porphyrin nanoparticles.


QN08.08.25

Block Copolymer Templated Nanostructured Metal Oxides Through Atomic Layer Deposition
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Design and engineering of metal oxide materials with controlled nanostructures present important applications in nanoelectronics and catalysis. Here we report a simple atomic layer deposition process to prepare uniform metal oxide nanostructures using self-assembled block copolymer polystyrene-b-polyvinylpyridine (PS-PVP) as the structure-directing scaffold. PS-PVP self-assembles in mixture of organic and water forming varied mesostructures such as micelles, tubes, and vesicles. These mesostructures have hydrophilic external interface that can further react with metal oxide precursors. Atomic layer deposition (ALD) was carried out to the hydrophilic interface of the mesostructures to grow metal oxide layers. Different oxides including TiO\textsubscript{2} and SnO\textsubscript{2} have been demonstrated at varied processing conditions. By altering ALD cycles, thickness of the metal oxide layer can be tuned. The capability of exerting rational control over dimension and composition of nanostructured metal oxides through ALD processes provides new opportunities in nanoelectronics and catalysis.

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

QN08.08.26

Increasing Magnetization in a Hollandite Multiferroic by Fe Doping—Structural, Magnetic and Dielectric Characterization of Nanocrystalline BaMnxFe3Ti4O12
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Device Lifetime Study of Colloidal Quantum Dot Light-Emitting Diodes

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Quantum dot light emitting diode (QD-LED) has attracted a great attention due to its high color purity, and solution processibility. However, understanding on how QD-LED fails is still lacking. Electroluminescence (EL) of QD in the sandwich structure between charge transport layers already reached 20% external quantum efficiency (EQE), but down conversion display is only available in the consumer market. Due to complex device architecture of QD-LED compared to down conversion type QD emitter, understanding how QD fails is challenging. In this study, we fabricated QD-LEDs with typical core/shell structure and our double heterojunction nanorod. We observed driving bias dependent device lifetime which reflect that there are universal degraded part in QD-LEDs. By measuring EL of QD-LEDs and PL of QD emitter film simultaneously, we revealed that QD film is still emitting PL despite of EL quenching. This clearly indicates that charge transport layer aging is main reason for the QD-LED degradation. Lastly, to overcome organic charge transport layer issue, we also suggested NiO hole transport layer to replace organic charge transport layer. By passivating NiO surface, device performance of NiO HTL based QD-LED was enhanced by factor of 5.

Binary and Ternary Metal Chalcogenide Nanoplates with Janus Structural Motif via Asymmetric Cation Exchange

Jongsik Park and Kwangyeol Lee; Chemistry, Korea University, Seoul, Korea (the Republic of).

Chemical transformations via postsynthetic modification of colloidal nanocrystals have largely investigated, because those approaches can provide an unusual route to elaborately composition-controlled nanostructures while maintaining the overall structure of template. In particular, the asymmetric cation exchange reaction could be achieved by imposing a significant kinetic hurdle to the cation exchange reaction. The different atomic arrangements of the core and crown in core-crown structures might further differentiate the surface energies of originally identical cation exchange sites, leading to different reactivities of these sites. Herein, we suggest that the synthesis of binary and ternary metal chalcogenide nanoplates with Janus structural motif via asymmetric cation exchange. This synthetic methodology exploiting cation exchange of surface-passivated semiconductor nanoparticles could fabricate the numerous symmetry-controlled Janus heterostructures.

Detection Limit of a Portable Raman Spectrophotometer for SERS Detection of GunShot Residue

Ellen Hondrogiannis, Mary Sajini Devadas, Evan Thayer, Wilson Turner and Dustin Baird; Department of Chemistry, Towson University, Towson, Maryland, United States.

The purpose of this work is the attribution of gunshot residue (GSR) to manufacturer using Surface Enhanced Raman Spectroscopy enabled by a bench top portable spectrometer. We propose nanostructures that span zero- (metal and magnetic clusters), one- (rods), and three- (microbars) dimensions, synthesized in our laboratory. These substrates are chosen because they have charge transfer capabilities with the organic analytes present in the GSR or electromagnetic field enhancements to provide a basis for this approach. This study presents the LOD measurements of the SERS signal from two organic compounds of GSR, diphenyl amine and ethyl centralite, with the gold and silver nanoparticles.

General Synthetic Strategy for the Fabrication of Cu-Based Bimetallic Two-Dimensional Hollow Nanostructures

Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., Columbus, Ohio, United States.

Bimetallic hollow nanostructures have become promising new candidates in biomedicine, fuel cells, and gas sensors due to their porous structures and the synergistic effect between two metals. Currently, galvanic replacement is a powerful strategy to fabricate bimetallic hollow nanostructures. However, most galvanic replacement literatures so far employ costly metal nanostructures as the template and involve complicated purification process. Here, we develop a one-step general synthetic method based on galvanic replacement for the fabrication of Cu-based bimetallic two-dimensional hollow nanostructures. Firstly, the copper nanosheets are prepared at 300 °C, and then metal ions (M = Au, Pt, Pd) with higher oxidation potential were injected into Cu nanosheets solution between 80 °C to 150 °C. Because Cu2+/Cu potential is less than that of M+/M, Cu atoms on nanosheets’ surface are replaced with M due to galvanic replacement; sequentially the interior Cu atoms will diffuse to outside owing to Kirkendall effect, which lead to the formation of hollow nanostructures. Compared to utilize other metal nanosheets as the template, our method consists of three advantages: 1. reduces the cost; 2. avoids the template separating process; 3. enriches two-dimensional bimetallic hollow nanostructures. These two dimensional hollow nanostructures with large surface area can be potentially used for the fabrication of gas sensors and as catalysts for converting CO to chemicals.

Stable Au-Pd Heterostructures for High Reflective Index Sensitivity

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Plasmonic noble metal nanoparticles show great promise in a variety of applications, ranging from theranostics to chemical sensing. Chemical sensing is possible through observing changes in the localized surface plasmon resonance (LSPR) in response to changes in environment. Au and Ag structures have notably high refractive index sensitivity (RIS), with Au structures typically being used for their greater structural stability relative to Ag. However, due to the high mobility of Au atoms, many structures degrade rapidly due to morphology changes. As we show, the RIS and structural stability of Au structures can be increased through the addition of Pd to such nanostructures. Specifically, Pd is directed to the tips of stellated Au nanostructures through kinetically controlled overgrowth. Interestingly, changing the capping agent switches the Pd deposition mode, producing stellated Au nanorods controllably coated with Pd. The RIS of these structures were measured by standard methods and compared to all-Au stellated structures. The results were analyzed as a function of structure (branching symmetry and particle size) as well as bimetallic distribution and Pd loading. This analysis is aided by simulations of the anticipated optical properties. This work is coupled with measurements of the brenchtop stability of structurally similar all-Au and Au-Pd stellated nanostructures. Collectively, this work demonstrates that the introduction of Pd to Au nanostructures both boosts RIS and structural stability, moving the design of LSPR sensors beyond the all-Au standard.

A Method for Quantification of Particle Shape in CMP Slurry and the Investigation for the Relationship Between the Polishing Behaviors and These Shapes

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The silicon wafers used as substrates for semiconductor devices are required to be of increasingly stringent quality because of the downscaling of these devices. Particularly, the
wafer surface quality, including the flatness and the local roughness, is critical in avoiding defects in the final products. These necessary surface perfections are achieved via chemical mechanical planarization (CMP) in the wafer manufacturing process, and repeatedly during both FEOL and BEOL flows to maintain global planarity between unit process steps. The SEM images were analyzed by Image J, with background modification and binarization by auto setting of local threshold using the Otsu method, and some overlapped edges were separated using Watershed method. Using this optimized filtering and detection process, it was possible to differentiate the edges of even the particles that were overlapped. Image analysis time was also decreased 1/5 by building a macro for these processes. The wafer polishing quality (the removal rate) was determined and compared with key particle shape values (diameter, particle size distribution, area, circularity etc…). The removal rate decreased when the particle ovality approached that of a perfect Circle. It seems that the surface oxidation as a chemical effect by particles decreased because the surface area of particles is lowest for a perfect sphere. However, there weren’t any significant differences found relating the wafer quality and the other particle shape values. More subtle effects based on these parameters might be obtained using a more sophisticated analysis method, such as a multiple regression analysis.

In conclusion, by optimized the processing method using the Image J, the quantitative value of particle parameters could be calculated from SEM images, while also improving the overall accuracy with less processing time. More subtle effects based on these parameters might be obtained using a more sophisticated analysis method, such as a multiple regression analysis.

Clustered Magneto-Plasmonic Nanoparticles for Amplified Surface Enhanced Raman Scattering Bio-Imaging

The removal rate decreased when the particle circularity approached that of a perfect Circle. It seems that the surface oxidation as a chemical effect by particles decreased because the surface area of particles is lowest for a perfect sphere. However, there weren’t any significant differences found relating the wafer quality and the other particle shape values. More subtle effects based on these parameters might be obtained using a more sophisticated analysis method, such as a multiple regression analysis.

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Clustered Magneto-Plasmonic Nanoparticles for Amplified Surface Enhanced Raman Scattering Bio-Imaging

Although many gold-based nanoparticles display strong NIR LSPR absorption properties and corresponding heat conversion efficiencies (HCE) as high as 80%, they are costly to produce and their size often exceeds 100 nm, a contentment trait in the context of most biological applications. Moreover, prolonged exposure to heat can result in the modification of the gold nanoparticles’ morphology, leading to changes in their LSPR absorption profile and a partial or complete loss of the heat conversion properties. These limitations are overcome with copper sulfide plasmonic nanoparticles. They absorb light over a broad NIR spectral range, are smaller, stable under prolonged optical excitation, significantly less expensive to synthesize, and display nearly analogous heat conversion capabilities compared to gold nanoparticles.

In this work, a straightforward method to synthesize monodisperse PEGylated copper sulfide nanoparticles of pure covellite (CuS) phase, featuring strong localized surface plasmonic resonance absorption in the near-infrared and flexible surface chemistry, imparted by monomethyl ether polyethylene glycol molecules, is developed and optimized. These nanoparticles show a remarkable photothermal heat conversion efficiency (HCE) of 71.4% -evaluated in water upon laser excitation at 806 nm—, which is among the highest for CuS systems and rivals that of plasmonic noble metal nanostructures.

A specific merit of the proposed green synthesis approach resides in the dispersibility of the CuS nanoparticles in water and media mimicking biological fluids. A prominent advantage of these nanoparticles as photothermal agents is represented by the minimal amount of optical energy scattered or re-emitted through luminescence, leading to nearly absolute conversion of light into heat.

Altogether, the properties featured by the developed CuS nanoparticles (small size, size monodispersity, colloidal stability in biological media, tunability of the surface chemistry, and outstanding light-to-heat capability) make the system an ideal candidate for a stand-alone photothermal agent and/or a valuable building block for multipurpose biomedical nanomaterials. Another relevant finding for the photothermal community, stemming from a critical evaluation and mathematical modeling of the material’s properties and measurement methodology, is that calculated HCE values drastically depend on the parameters characterizing the experimental setup used to determine them. In particular, the dependence on the solvent absorption and other experimental conditions, such as sol concentration and optical path, calls for some degree of standardization on the measurement of HCE for potential photothermal agents in order to make the data reported universally and reliably comparable.
Raman scattering (SERS) effect simultaneously. Plasmonic nanostructures have attracted much attention due to SERS effect. The areas with localized and enhanced electromagnetic field become “hot spots” where show high SERS activity. Recently, Raman reporter-embedded plasmonic nanostructures have been investigated for advanced signal reproducibility and sensitivity [1] which are affected by uniformity of morphology and size. [2] However, magneto-plasmonic nanoparticles have been rarely reported for SERS bio-applications. Thus, there is a great demand in synthesis of magneto-plasmonic nanoparticles as an attractive SERS nanoprobe.

Here we report a clustered magneto-plasmonic nanoparticle as a candidate for ultra-sensitive and stable SERS biosensing. Superparamagnetic iron oxide colloidal nanocrystal clusters (SPION-CNCs) which are about 150 nm in diameter are synthesized by modified polyol method without surfactant. The SPION-CNCs are composed of many primary particles approximately 10 nm in size to overcome superparamagnetic-ferromagnetic transition and particle aggregation problem. [3] Subsequently, we cover the thin SiO₂ layer onto the surface of SPION-CNCs. Au seeds (3~4nm) are attached onto the SiO₂ layer. For obtaining high signal reproducibility and sensitivity, we execute the homogeneous Au seed-mediated growth procedure. We confirm that Au nanoparticles are densely decorated on the shell after growth process with inter-spacing between Au nanoparticles of 1~2 nm. During the growth step, we conjugate the Raman reporter onto the surface of Au nanoparticles. As a result, the Raman dye-embedded magneto-plasmonic nanoparticles exhibit robust and ultra-sensitive SERS signals based on their uniform size, morphology and existence of abundant “hot spots”. Finally, we show that the magneto-plasmonic nanoparticles can be used efficiently for bio-imaging, bio-detecting and bio-separation about specific biomarkers. This nanoparticle with novel structure offers a great strategy for image-guided diagnosis and separation of target biomarker.


QN08.08.36
Optimization of Various EHD-Jet Spray Modes for QD Thin Films in Quantum Dots Light-Emitting-Diodes
Weon-Soon Choi and Canh Tuan Nguyen; Hoseo University, Asan, Korea (the Republic of)

In recent years, colloidal quantum-dots based light-emitting diodes (QD-LEDs) have been considered as the attractive display device because of remarkable electrical/optical characteristics of colloidal quantum-dots. QD-LEDs are of particular interest due to their wide-range color tune ability, high brightness and good color purity by narrow emission bandwidth. Challenges remain, however, in achieving the necessary multilayer device structures using printing process for display applications. Conventional vacuum evaporation deposition to fabricate QLEDs was unsuitable for heavy metal like QDs materials. Besides, the spin coating has been the most popular approach to fabricating QD-LEDs devices due to the simple method for achieving a near monolayer of the nanoparticle. However, the relatively high cost of QDs and the loss of more than 96% of the QD solution during spin coating are strong reasons to search for an alternative deposition route capable of patterning and consuming minimum amount of QD materials. QDSEs were synthesized with a trochoidal electrohydrodynamic (EHD)-jet spray technology and were applied to all solution-processed QD-LEDs. Three different spray modes of (i) ‘Big circular type’, (ii) ‘Spiral line’, and (iii) ‘Straight line’ were investigated to obtain uniform QD thin films. Sprayed QD pattern was also controlled with the various processing parameters to obtain uniform surface morphology. A QD-LED has a structure of ITO/PEDOT:PSS/PVK/ EHD-sprayed QDs/ZnO/Al. Using a unique spraying technique, a QD-LEDs was successfully fabricated and demonstrated a maximum of luminance of 7801 Cd/m², a maximum current efficiency of 2.93 cd/A, the maximum EQE is 1.41%. We believed that EHD jet printing will pave the way for the fabrication of multilayer structure devices, allowing for various solvents, toward to a direct patterning, and convenient and optimal for commercial production.

QN08.08.37
Novel Photocatalyst Gold Nanoparticles with Dumbbell-Like Structure and Their Superiorly Photocatalytic Performance for Ammonia Borane Hydrolysis
Zou Xiuxi, Zhu Mingyun and Dai Yunqian; Southeast University, Nanjing, China.

Gold nanoparticles (Au NPs) have attracted remarkable research interest in heterogeneous catalysis due to their unique physical and chemical properties. However, only small-sized Au NPs (<7nm) exhibit promising catalytic activity. In this work, dumbbell-like Au NPs (D-Au NPs) with an average size of 37 x 11nm were prepared by a secondary seed-mediated growth method to serve as novel photocatalysts for ammonia borane (AB) hydrolysis. A maximum of luminance of 7801 Cd/m², a maximum current efficiency of 2.93 cd/A, the maximum EQE is 1.41%. We believed that EHD jet printing will pave the way for the fabrication of multilayer structure devices, allowing for various solvents, toward to a direct patterning, and convenient and optimal for commercial production. The electrical properties of flexible nano-metal polymer were tested and the highest improvements in breakdown strength and energy density of 33 and 58 %, respectively were measured with 0.05 wt.% Ag content and APS as a stabilizer.

QN08.08.38
Impact of Stabilizer on In Situ Formation of Ag Nanoparticles in Polyvinylidene Fluoride (PVDF) Matrix
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Materials based on nanometer-sized metal particles have received increasing attention due to their novel electronic, magnetic, and optical properties. Metallic nanoparticles have a wide range of applications in biomedicine, optoelectronics, energy, and industrial applications such as catalysis, automotive, aerospace and electronic components. Finely-dispersed metallic nanoparticles in a polymeric matrix can act as dielectric insulators due to their small size and very low surface charges. Achieving a uniform dispersion of nanoparticles in the polymer is a crucial step to obtain the optimal electrical properties for the given nanocomposite. In this research work, In situ synthesis of Ag nanoparticles in polyvinylidene fluoride (PVDF) was investigated using different stabilizers such as 3-aminopropyltrimethoxysilane (APS) and 1-dodecanethiol (thiol). Although PVDF is a matrix, it also functions as a stabilizer. Results of UV-vis spectroscopy showed that when APS or PVDF was used, Ag nanoparticles were formed. Yet no formation occurred when thiol was used due to the complexion of Ag+ ions by thiol. Polar groups on stabilizers has an important effect on complexion process. APS, a nitrogen-based ligand, has hard base character inhibiting the complexion of Ag+ and APS. Consequently, Ag+ ions are reduced to Ag nanoparticles in N,N dimethyl formamide (DMF), which acts as a solvent and reducing agent. The electrical properties of flexible nano-metal polymer were tested and the highest improvements in breakdown strength and energy density of 33 and 58 %, respectively were measured with 0.05 wt.% Ag content and APS as a stabilizer.

QN08.08.39
Silver Chalcogenide Colloidal Quantum Dots for Room Temperature Photodetection in the Mid-Wavelength Infrared
Shihab Haflı1, Michael Scimeca1, Peter Zhao2,3, Ayasakata Sahu1 and Dong Kyun Ko2; 1Department of Electrical and Computer Engineering, New Jersey Institute of Technology, Newark, New Jersey, United States; 2Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, New York, United States; 3Department of Chemical Engineering, Cooper Union, New York, New York, United States.

Lately discovered silver chalcogenide colloidal quantum dots with tetragonal crystal phase exhibit promising optical properties in the mid-wavelength infrared. Although colloidal synthesis of uniform sizes and shapes has been reported, the investigation of their optoelectronic properties as an active layer in photodetector devices has been scarce. Herein, we present silver selenide quantum dot photoconductive photodetectors that exhibit high responsivity in the mid-infrared under room temperature operation. We investigate the effect on the ligands as well as bias-, temperature- and spectral-dependent photoresponses. Our work demonstrates the potential of silver chalcogenide colloidal quantum dots as an promising mid-wavelength infrared absorber for the development of thermal infrared sensors and imagers with low size, weight, power consumption, and cost.

QN08.08.40
Omnidispersible Hedgehog Particles with Multilayer Coatings for Multiplexed Biosensing
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Hedgehog particles (HPs) resembling the spiky geometry of pollen grains reveal surprisingly high dispersion stability in both polar and nonpolar media. This property designated
as omnidispersibility, is attributed to the substantial reduction of van der Waals interactions between particles coated with stiff nanoscale spikes compared to particles of the same dimensions with smooth surfaces. One may hypothesize but it remains unknown, however, whether HPs modified with polymers or nanoparticles (NPs) would retain this property. Such modifications will expand the functionalities of HPs making possible their utilization as omnidispersible carriers. We show that HPs carrying dense conformal coatings made by layer-by-layer (LBL) assembly maintain dispersion stability in environments of extreme polarity and ionic strength. Additionally HPs, surface-modified by multilayers of polymers and gold NPs are capable of surface enhanced Raman scattering (SERS) and overcome the limited colloidal stability of other SERS probes. The agglomeration resistance of HPs leads to greater than one order of magnitude increase of SERS intensity compared to colloids with smooth surfaces and enables simultaneous detection of several targets in complex media with high ionic strength. Omnidispersible optical active colloids open the door for rapid multiplexed SERS applications in biological fluids and other applications.

QN08.08.41
Conductive Nanoparticle Superlattices Grow—Insights from In-Situ Real-Time X-Ray Scattering at the Liquid/Air Interface Santanu Maiti1*, Alexander Andre, Somi Maiti, Jan Hagemöcher, Andre Maier, Rupak Banerjee, Andrei Chumakov, Oleg Kovalov, Marcus Schelle and Frank Schreiber2*
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Directional cross-linking of organic semiconductors (OSC) with nanocrystals (NC) produces superlattices exhibiting novel structural and electronic properties1–2. Here, we discuss the kinetics of spherical PbS NCs during self-assembly and ligand exchange to form coupled organic-inorganic superstructures (COINS) at the liquid/air interface, monitored by in-situ grazing incidence small angle X-ray scattering (GISAXS)1. Finally, we present the result on the in-situ formation of conductive, iso-oriented mesocrystalline superstructures with cubic PbS NCs at the air-liquid interface, investigated simultaneously by GISAXS and grazing incidence X-ray diffraction (GIXD) in real-time3–5. In both cases, we observe a continuous contraction of superlattices with elapsed time, preserving their superlattice symmetries (bcc for spherical and sc for cubic shape NCs). We attribute these contractions to the complete replacement of native oleic acid ligands with small OSC cross-linkers like tetrabutylammonium tetrathiafulvalene-carboxylate (TTFDA), cobalt/copper 4,4’,4”,4'''-tetraaminophthalocyanine (CoTAPc/CuTAPc). Such investigations provide crucial visualizations into the formation mechanism of such nanostructures, which already find practical applications.

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QN08.08.42
Simple Microwave-Assisted Synthesis of Fluorescent and Multi-Functional Carbon Quantum Dots from Polyamidation Monomer Set Binhee Kwon, Insik In, Geumbi Jeong, and Soongmin Park; Korean National University of Transportation, Chungu-si, Korea (the Republic of).

Recently, carbon quantum dots (CQDs) have been received considerable attentions due to their fascinating optoelectrical properties and inherent non-toxicity to human bodies and environments. Synthetic approaches of alternative materials of semiconductor or inorganic quantum dots (QDs) in many applications. Various synthetic protocols such as top-down and bottom-up have been proposed to synthesize highly fluorescent CQDs from a variety of starting materials. Among these, microwave-assisted bottom-up synthesis of CQDs have several outstanding benefits because various natural or synthetic ABx or Ax/By polyamidation monomer set (A: -COOH, B: -NH2) could be utilized to formulate CQDs with control of their surface functionalities and high fluorescent within short microwave operation time less than 10 min. The construction of CQDs from polyamidation monomer sets is regarded to proceed through both polyamidation and carbonization and it has been confirmed that polyamidation monomer sets possessing ‘branching point’ are suitable for the facile synthesis of CQDs. Synthesized CQDs are soluble in solvent media, highly nontoxic in physiological environments, strongly fluorescent, which is revealing that CQDs can be exploited as various applications including fluorescent cellular imaging, photocatalysis, fluorescence on/off sensors, up-converting top layers on solar cells, drug-delivery systems, fluorescent polymer nanocomposites, etc.

QN08.08.43
Thermal Excitation Control of Instantaneous Photon Emission in Semiconductor Nanocrystals Benjamin T. Diroll; Argonne National Laboratory, Lemont, Illinois, United States.

Photon emission from many materials at low temperature is governed by optically passive “dark” states. For example, cadmium selenide nanocrystals are observed to have “dark exciton” photoluminescence lifetimes of 1 microsecond at liquid helium temperatures. This work presents ultrafast photoluminescence spectroscopy which demonstrates that an electronic excitation followed by subsequent, time-delayed IR excitation of cadmium selenide nanocrystals converts excitons from the “dark” state, with slow emission, to the spin-allowed “bright” exciton state, which increases the instantaneous rate to <100 ps. The IR control pulse excites organic ligand molecules on the nanocrystal surface, which act as antennae, leading subsequently to heat transfer to the inorganic particle. The IR control pulse can be arbitrarily delayed to induce changes in the instantaneous rate with less than 10 ps temporal resolution. This technique has the ability to dramatically re-shape the distribution of photon emission events in ensembles and single photon sources.

QN08.08.44
Biosynthesis of Functionalized Green Gold Nanoparticles Using a Hydroxylated Tetraterpenoid for Anti-Cancer Applications Jiulong Li1,2, 1Northeastern University, Boston, Massachusetts, United States; 2Zhejiang University, Hangzhou, China.

Colloidal Nanoparticles (e.g., gold nanoparticles) are a type of especially promising candidate nanomaterials in nanomedicine due to their ease of synthesis, versatility in surface modification and relative cytocompatibility. Functionalized AuNPs are especially useful for therapeutic strategies for cancer. Understanding the synthesized mechanisms and cell–nanoparticle interactions are important for the use of AuNPs. Here, we detail the biotransformation mechanism of Au(III) into AuNPs using hydroxylated deinoxanthin (DX) from the extremophile Deinococcus radiodurans based on the results of HR-TEM, EDS, FTIR, NMR, XPS and LC-MS. The biosynthesis of DX–AuNPs was attributed to the deprotonation of the hydroxyl groups of DX. The deprotonated 2-ketodeinoxanthin (DX3) served as a capping agent to stabilize the AuNPs. The functionalized DX–AuNPs exhibited significant anticancer activity by altering gene expression levels and regulating cell membrane integrity and metabolism, increasing ROS generation, autophagy, and apoptosis in cancer cells. These novel findings provide significant insight into the biomimicking mechanism of green AuNPs functionalized with natural products, which possess enhanced anticancer activity. The biomedical AuNPs could have therapeutic potential in the treatment of cancer, as well as numerous other medical applications.

QN08.08.45
Fabrication of Gold Nanoparticles of Different Sizes and Its Interaction in Aquatic Phase Rosymer Rivera-Colón and Sonia J. Bailón-Ruiz; Chemistry, University of Puerto Rico in Ponce, Ponce, Puerto Rico.

Gold nanoparticles (AuNPs) are highly used in recent times due to their fascinating optical properties. AuNPs have several applications in the medical context as drug delivery, antimicrobial activity, anti-fungal, diagnoses, tissue engineering, regenerative medicine and therapeutic treatments such as cancer. One of the most remarkable phenomena that these nanoparticles have is the collective oscillation of their conduction band electrons when these electrons are illuminated with an appropriate wavelength. This phenomenon is known as Surface Plasmon Resonance, which confer intrinsic optical properties to the AuNPs. Due to the massive use of these nanoparticles in the world, eventually these nanostructures will be interacting with body waters including the sea and it could be causing negative effect in marine organisms. Based on the mentioned, the objectives of this study were (i) synthesize gold nanoparticles of different sizes in presence of sodium citrate, (ii) characterize the morphology and optical properties of AuNPs and, (iii) evaluate the interaction of synthesized nanomaterials in marine crustaceans. The generation of AuNPs was realized in presence of gold solution (Au⁺), and citrate solution as reducing agent. The precursors were heated at 100°C by using a hot plate and stirred for 10 minutes. The production of AuNPs was proved by the color change in the solution; from yellow to red wine. Purified nanoparticles by dialysis membranes, evidenced an absorption peak at 523 nm attributed to the surface Plasmon Resonance which suggested the formation of gold.
Semiconductor nanomaterials like zinc sulphide have interesting potential applications, consequent to their size-dependent optical properties. These nanostructures can be used on optoelectronic, photocatalysis, solar cells, and fluorescence microscopy, among others. Due to the great use of these nanoparticles in society, there is great concern in the scientific community about the potential negative interaction of these nanomaterials in aquatic environments. The present research was addressed on generation of nanostructures of ZnS with modified surface. This work had three goals: 1) morphological, compositional and optical characterization of ZnS nanoparticles; 2) surface chemical modification of ZnS nanoparticles with biocompatible molecules; and 3) interaction studies of ZnS nanoparticle. A main absorption peak at ~350 nm and a trap emission peak at ~425 nm were observed in the emission spectrum of ZnS nanoparticles. The morphology and the size of ZnS were carried out by High Resolution Transmission Electron Microscopy (HR-TEM). In this way, nanoparticles were spherical and with a size around 5 nm. Energy Dispersive X-Ray Spectroscopy evidenced the chemical composition of produced nanostructures. The chemical modification of ZnS nanostructures was corroborated by Infrared Spectroscopy Analysis. The interaction of nanoparticles of ZnS was studied in aquatic systems in presence of marine organisms. The concentrations of nanoparticles for the interaction studies ranged from 0 ppm to 2000 ppm and the contacting time was 24 or 48 hours. Also, ZnS (as zinc nitrate and zinc sulphate) was used as comparison purposes. The results evidenced that ionic Zn (as zinc nitrate and zinc sulphate) had a negative interaction in marine organisms at concentrations higher than 500 ppm, whereas Zinc sulphide nanoparticles evidenced a negative interaction only at concentrations higher than 1000 ppm. The chemical interaction between the type of organic cover of ZnS and the marine organisms will be discussed.
The self-assembly of colloidal nanocrystals (NCs) into superstructures provides an efficient bottom-up pathway for constructing new functional materials. Among various superstructures, NC superlattices represent an entirely new class of solid-state materials with unique collective properties and wide applications. However, conventional NC superlattices are inappropriate structural motifs for energy applications due to the impeded molecular accessibility of NCs by foreign species. In pursuit of widening the range of applications of NC superlattices, it is desirable to develop new architectures that enable full access of NC constituents while simultaneously facilitating mass transport properties. Herein, I will focus on low-dimensional, hierarchical NC superlattices with rationally designed structures and mesoscale morphologies toward high-performance energy storage and conversion. I will also spend half of the time to cover NC superlattice derivatives, especially ordered graphene-like frameworks, which are emerging as a new class of mesoporous carbon materials. By exploiting the versatile surface chemistry and self-assembly behaviors of colloidal NCs, a rich array of mesoporous graphene-like materials can be designed, which show great promise as material platform for energy applications.

Aqueous Synthesis of CuZnSnS and CuZnSnSe Nanoparticles for use in Next-Generation Solar Cells

Metal chalcogenide semiconductors continue to show promise as potential scalable, cheap, and tunable metal chalcogenide-based photovoltaics (PV). Among these, the quinary I_2-IV-III-VI_3 family, which includes CuZnSnS (CZTS), CuZnSnSe (CZTSe), and CuZnSn(S/Se)_4 (CZTSSe), are among the most lucrative due to their earth-abundant and non-toxic nature. The fabrication of such materials using nanoparticle routes remains among the most promising for PV due to their potential to be inexpensive and scalable, while maintaining superior phase and compositional control when compared to non-solution based approaches. Here we describe the facile synthesis of aqueous CZTS and CZTSe nanoparticles through a versatile, stoichiometric, one pot synthetic method that produces scalable dispersions without the use of long-chained organic ligands. These materials lend themselves toward the fabrication of carbon-free absorber layers for solar cells. Towards this goal, here we describe a simple process to produce CZTSSe by depositing mixed amounts of CZTS and CZTSe nanoparticle inks followed by a mild heat treatment. The resulting materials exhibit a single-phase kesterite structure and tunable optical bandgaps of between 1.51 and 1.05 eV, which are ideal for single and multi-junction solar cell devices.

The Best of Both Worlds—Merging the Plasmonic Properties of Silver with the Functionality of Gold via Living Reaction Conditions

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This will talk will provide an overview of our recent developments in the design of nanomaterials for ultrasonic biosensing. Bio-responsive nanomaterials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering (1). Using enzyme-mediated signal readouts we have developed a suite of nanoparticle based ultrasonic biosensing assemblies as well as a cell/tissue-interfacing nanoneedle platform (2). We are applying these biosensing approaches both in high throughput drug screening and to diagnose diseases ranging from cancer to global health applications.


2:30 PM *QN08.10.03 Driving Forces for Oriented Attachment-Based Crystal Formation and Assembly Xin Zhang1, Byunghan Kim2, Yu-Ting Liao3, 4, Sonia Castellanos Ortega4, Alberto Salleo5, and Paul Alivisatos1, 2, 3.

Driving forces for oriented crystal formation and assembly depend on the structure and alignment of the surfaces. The driving forces can be sensitive to relative orientation include Coulombic, van der Waals (vdW), hydration, and ion correlation forces. The theoretical underpinnings of these anisotropic forces are well established, but techniques that can directly measure them for a given pair of interacting oriented crystal faces have generally been limited to use of macroscopic yet atomically flat single crystals. We report measurement of anisotropic forces between rutile TiO2 (001) nanocrystals as a function of their azimuthal orientation and surface hydration extent using a combined environmental transmission electron microscopy-atomic force microscopy (AFM) technique. Atomically flat rutile TiO2 (001) AFM tips and opposing rutile TiO2 (001) substrates were fabricated by focused ion beam milling to excite nanocrystals from the surface of a single monolith that was pre-oriented, cut, and polished to prepare the (001) face. At tens of nanometers of separation, the attractive forces are weak and show no dependence on azimuthal alignment nor surface hydration. At separations of approximately one hydration layer, attractive forces are strongly dependent on azimuthal alignment and systematically decrease as increasing water density increases. Measured forces closely agree with predictions from Lifshitz theory and show that dispersion forces are capable of generating a torque between particles interacting in solution and between grains in materials. Furthermore, we report the measurement of anisotropic forces between ZnO (0001) and ZnO (0001) nanocrystals in Zn(NO3)2 solution using AFM-based dynamic force spectroscopy (DFS). By measuring the jump-from-contact force as a function of tip retraction rate, the rupture force at equilibrium and the corresponding adhesion free energy as a function of azimuthal alignment is directly obtained. Compared with the potential of mean force (PMF) from large-scale molecular dynamics (MD) simulations, the sensitivity to crystallographic registry between nanocrystals at close range arises, at least in part, from the self-organization of interfacial water molecules in response to the structures and alignment of the opposing surfaces.

3:00 PM BREAK

3:30 PM *QN08.10.04 Synthesis of Porphyrin Nanocrystals and Applications Feng Bai; Henan University, Henan, China.

Abilities to control the size and shape of nanocrystals in order to tune functional properties are an important grand challenge. Here we report a surfactant self-assembly induced micelle encapsulation method to fabricate porphyrin nanocrystals using the optically active precursor zinc porphyrin (ZnTPP). Through confined non-covalent interactions of ZnTPP within surfactant micelles, nanocrystals with a series of morphologies including nanodisk, tetragonal rod, and hexagonal rod, as well as amorphous spherical particle are synthesized with controlled size and dimension. A phase diagram that describes morphology control is achieved via kinetically controlled nucleation and growth. Due to the hierarchical ordering of the porphyrins, the nanocrystals exhibit production and PTCD for cancer. This simple ability to exert rational control over morphology provides new opportunities for practical applications in photocatalysis, sensing, and nanoelectronics.

4:00 PM *QN08.10.05 Metal Nanoclusters and Nanoparticles Tethered by N-Heterocyclic Carbene-Capped Polymers Jie He; University of Connecticut, Storrs, Connecticut, United States.

N-heterocyclic carbenes (NHCs) are excellent ligands that bind to a variety of metal ions in Group 10/11 with extremely high binding strength via π donation. However, there are only a few studies of polymer NHCs that for metal nanoparticles (NPs) in literature, largely due to synthetic challenges of carbine, in particular under aqueous conditions. We present a new method to synthesize metal nanocluster and NPs with NHC-functionalized polymers as surface ligands. Two approaches will be discussed in this talk, including in situ reduction and transmetalization. NHC-functionalized polymers can be prepared using simple post-polymerization functionalization of polymers capped with halogen atoms (e.g., Cl and Br) synthesized via atom transfer radical polymerization (ATRP). When reacted with N-methyl imidazole, halogen-ended polymers can be converted to yield imidazolium salt and further transferred into Cu(NHC)2 complexes in the presence of a weak base, e.g., K2CO3 and CuCl2. We first show that Cu-NHC-polymer can be reductively chemically in solution to form Cu nanocrystals with the bright blue fluorescence. Polymer NHC ligands can stabilize Cu nanoclusters from oxidation as well. In the second approach, we demonstrate that Cu(NHC)2 complexes can be used to modify metal NPs using transmetalization in any good solvents of polymers. The surface modification of citrate-capped gold NPs has been examined using a ligand exchange method in an emulsion solution. We show the successful surface modification of Au/Au/Cu NPs using both approaches, providing collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photocatalytic degradation of methyl orange (MO) pollutants, hydrogen production and PTCD for cancer. This simple ability to exert rational control over morphology provides new opportunities for practical applications in photocatalysis, sensing, and nanoelectronics.

4:30 PM *QN08.10.06 Direct Patterning of Quantum Dots on the Nanoscale with E-Beam Lithography Christian D. Dieleman1, Weiwei Ding1, Sonia Castellanos Ortega2, and Bruno Ehrler1; 1AMOLF, Amsterdam, Netherlands; 2Advanced Research Center for Nanolithography, Amsterdam, Netherlands.

Interaction with light on the nanoscale is a very active research field, nanophotonics. Commonly, these nanostructures are made from metallic or dielectric materials, while nanostructures from active materials such as semiconductors, for example used for making integrated circuits, require intricate lithography with photoresists as an intermediate step. Here we show that Colloidal Quantum Dots (CQDs) can be used to directly write patterns on the nanoscale from the active semiconductor material. CQDs are nanocrystals of semiconductor materials, owing their tunable optical, chemical, and electrical properties to quantum confinement size effects and surface chemistry. These tunable properties make CQDs useful for different semiconductor applications including photovoltaics and lighting. We directly pattern quantum dots using e-beam lithography in order to obtain high-resolution nanodevices of CQDs at the nanoscale. This technique is applicable to different QD systems, such as CdSe and PbS without affecting the luminescent properties. We present several examples of nanostructures and show that the resolution can be on the order of tens of nanometers. The chemical mechanism responsible for the observed solubility switch is investigated. We believe this technique shows promise for manufacturing of photonic structures at high volume, directly from the active materials.

4:45 PM *QN08.10.07 Understanding the Synthetic Pathways and Developing Techniques to Probe the Rare Non-Radiative Events in CdSe/CdS Colloidal Quantum Dots with Photoluminescent Quantum Yields Approaching Unity Brent A. Koscher1, 2, David Hanifi1, Noah Bronstein1, 2, Zachary Nett1, 2, Joseph Swabeck1, 2, Kaori Takano1, 3, Koen Vandewal1, 3, Yoeri van de Burg1, Alberto Salleo2, 3, and Paul Alivisatos2, 3; 1University of California, Berkeley, Berkeley, California, United States; 2Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Stanford University, Stanford, California, United States; 4HPM Research & Development, High Performance Materials Company, JXTG Nippon Oil & Energy Corporation, Yokohama, Japan; 5Hasselt University, Diepenbeek, Belgium; 6Eindhoven University of Technology, Eindhoven, Netherlands.
Unconventional Templated Synthesis of Coupled Magnetic-Plasmonic Nanostructures

Zhihao Zhao, Xinran Chamele, Yu Yao, Michael Kozicki and Chao Wang; Arizona State University, Tempe, Arizona, United States.

Counterfeit goods have become a global issue that costs tremendous economic loss and security problems. Here we report on a one-pot photochemical synthetic method to produce dendritic silver nano-particles (AgNPs) promising for physical taggants. Unlike conventional techniques such as holograms and DNA signatures, this method can readily generate large quantities of dendritic AgNPs in 20 minutes under UV illumination and ambient conditions, which possesses great economic value and is desired for large-scale manufacturing. The interplay between silver nucleation and growth could significantly afect the product shape and size. We demonstrate that the tuning of experimental conditions, such as the UV illumination time and the concentration of reducing agent, poly(allylamine), indeed creates unique dendritic structures with distinctive morphological characteristics. All the dendrites possess a singular set of minutiae that lead to a vast number of unclonable features. As the AgNP sizes reach 10-100 μm, the structural information may be quickly read and analyzed by optical microscopy, which has great potential for anti-counterfeiting labels in supply chains.

9:30 AM QN08.11.05

Unconventional Templated Synthesis of Coupled Magnetic-Plasmonic Nanostructures

Zhixue Li and Yadong Yin; University of California, Riverside, Riverside, California, United States.
The promising of anisotropic plasmonics in state-of-art researches lies in orientational control of nanostructures, which is most invariably based on substrate regulation or single-structure measurements. Magneto-optics enables active control yet is lacking general approach towards multifunctional nanostructures. Herein, we report an unconventional templated approach towards coupled magnetic-plasmonic nanostructures. Particularly, the magnetic nanorods inside templates not only regulate the seeded growth but also provide magnetic tunability of their optical properties. By controlling the repining of small Au seeds during the early stage of crystal growth, hybrid Au/Fe₃O₄@Au core/shell nanostructures can be produced. This approach can be extended to different metallic nanostructures, like Ag or Cu, other shapes (plates, rods or cubes) or sizes. The plasmonic peak positions of coupled nanostructures can be tuned from visible to infrared region while their absorption/scattering can be finely tuned by the thickness of the metallic nanostructures during synthesis. More interestingly, their physical properties, like plasmonic excitation modes, optical scattering and photothermal conversion can be readily controlled by a magnet, providing vast opportunities for smart nanomaterials. For example, by controlling their orientation in polymer films, they can sense both linear (rotating and bending) and non-linear (twisting) mechanical perturbations. Also, magnetic tuning provides active modulation of imaging signals for biological background-free imaging, which can either enhance or suppress the contrast signals on demand.

9:45 AM BREAK

10:15 AM QN08.11.06

Ligand Effects on Nucleation, Growth and Size Focusing of Colloidal Metal Nanoparticles Ayman M. Karim; Virginia Tech, Blacksburg, Virginia, United States.

Colloidal synthesis of metal nanoparticles has shown tremendous control over size and shape. Understanding how ligands affect nucleation and growth is crucial in controlling size, shape and their distributions. In this talk we show experimental results elucidating the crucial role ligands play in controlling the rates of nucleation and growth and how the ligands contribute to size focusing during the synthesis of Pt and Ir nanoparticles. Using in-situ small angle x-ray scattering, isothermal titration calorimetry and density functional theory calculations, we measured the rates of nucleation and growth, and the M-L binding energies (M = Pt or Ir and L is the ligand) for different ligands. We show that the rates of nucleation and growth are correlated with the M-L binding energies for the metal precursor and metal nanoparticle, respectively. Interestingly, the correlation between nucleation and growth rates and M-L binding energies appears to follow a Brønsted-Evans-Polanyi (BEP) type linear relationship. Moreover, using population balance kinetic modeling, we demonstrate that size focusing of colloidal nanoparticles is largely due to growth rate constant that decreases with ligand coverage on the surface of the nanoparticles through a BEP relationship. This makes growth slower on larger nanoparticles (due to higher coverage), allowing the smaller ones to catch up, thereby focusing the size distribution. The consequences of the M-L binding strength on the size and size distribution will be discussed in relationship to our results and the literature.

10:30 AM QN08.11.07

Competition of Charge and Energy Transfer Processes in Donor-Acceptor Fluorescence Pairs—Calibrating the Spectroscopic Ruler Pavel Moro1, Zhicheng Jin2, Hedi Mattoussi3 and Mikhail Zamkov4; Bowling Green State University, Bowling Green, Ohio, United States; 2Florida State University, Tallahassee, Florida, United States.

Sensing strategies utilizing Förster resonance energy transfer (FRET) are widely used for probing biological phenomena. FRET sensitivity to the donor–acceptor distance makes it ideal for measuring the concentration of a known analyte or determining the spatial separation between fluorescent labels in a macromolecular assembly. The difficulty lies in extracting the FRET efficiency from the acceptor-induced quenching of the donor emission, which may contain a significant non-FRET contribution. Here, we demonstrate a general spectroscopic approach for differentiating between charge transfer and energy transfer (ET) processes in donor–acceptor assemblies and apply the developed method for unraveling the FRET/non-FRET contributions in cyanine dye–semiconductor quantum dot (QD) constructs. The present method relies on correlating the amplitude of the acceptor emission to specific changes in the donor excitation profile in order to extract ET-only transfer efficiencies. Quenching of the donor emission is then utilized to determine the non-ET component, tentatively attributed to the charge transfer. We observe that the latter accounts for 50–99% of donor emission quenching in QD-Cy5 and QD-Cy7 systems, stressing the importance of determining the non-FRET efficiency in a spectroscopic ruler and other FRET-based sensing applications.

10:45 AM QN08.11.08

Colloidally Synthesized Silicon Triplet Photosensitizers for Photon Upconversion Tingting Huang and MingLee Tang; Chemistry, University of California, Riverside, Riverside, California, United States.

Silicon is non-toxic, earth abundant, easily available and can be safely excreted by mammals. These features make silicon nanoparticles very attractive for biomedical applications. Silicon nanostructures have historically been underexplored for their ability to electronically communicate with molecules. In fact, molecular modification of silicon has mostly served to alter the surface energy of single crystal or nanosporous silicon. In contrast, here, colloidally synthesized silicon nanoparticles are explored as the light absorbers responsible for the sensitization of molecular triplet states. Fusion of these spin-triplet excited states create photons higher in energy than the original excitations in the form of spin-singlet excited states. This talk will focus on the low temperature synthesis of nanosized silicon colloid photosensitizers for photon upconversion based on liquid silicon halide precursors in combination with amine-based transmitterligands, building on conditions established by Rongchao Jin’s and Susan M. Kauzlarich’s group. Comparison to the lanthanide nanoparticles used for photon upconversion that usually result in drastic heating will be made.

11:00 AM QN08.11.09

Synthesis and Photophysical Properties of Complex Heterostructures Comprised of Epitaxially-Connected Domains of Materials with Disparate Lattice Structures Vladmir Savevich, Tom Nakotte, Oleg Kozlov, Jeongkyun Roh, Rohan Singh and Victor Klimov; Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Rational design of nanocrystals (NCs) can lead to material systems with fascinating properties. The combination of different materials in single crystalline heterostructures with precisely tunable properties, size and domain functionalities represents a powerful approach for creating novel functional building blocks with tuned electronic energy charge relaxation dynamics. These nanoblocks become a unique platform for exploring fundamental semiconductor physics at the nanoscale and can be used to fabricate novel materials with controllable application-targeted characteristics. Here we report a novel synthetic approach to achieving high-quality heterostructures based on epitaxially joined semiconductor and metal components. Importantly, this synthetic technique enables us to tackle a long-standing problem of uniform epitaxial shell growth around irregularly faceted NCs including synthesis of core/shell nanostructures with an extremely large lattice mismatch. In one example, we target an "inverted" CdSe/PbSe quasi-type II structure wherein an electron is delocalized across the entire NC while a hole is responsible for the sensitization of molecular triplet states. Fusion of these spin-triplet excited states create photons higher in energy than the original excitations in the form of spin-singlet excited states. This talk will focus on the low temperature synthesis of nanosized silicon colloid photosensitizers for photon upconversion based on liquid silicon halide precursors in combination with amine-based transmitter ligands, building on conditions established by Rongchao Jin’s and Susan M. Kauzlarich’s group. Comparison to the lanthanide nanoparticles used for photon upconversion that usually result in drastic heating will be made.

11:15 AM QN08.11.10

References:
Reversible Polarized Optical Response of Stretched Shape Memory Polymers with Embedded Gold Nanoparticles Prachi R. Yadav, Sumeet R. Mishra, Brian S. Chapman, Brian B. Lynch, Amy L. Oldenburg and Joseph B. Tracy; Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States; Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Polymer nanocomposites with embedded functional nanoparticles (NPs) are a rich and complex system, where the polymer can drive assembly of the NPs, and the NPs can be used to actuate the polymer. When plasmonic NPs, such as Au NPs, are dispersed within polymers, their organization determines the interparticle distances and extent of coupling of their surface plasmons. The objective of this study was to investigate plasmon coupling of spherical Au NPs with an average diameter of 17 nm in shape memory polymer (SMP) films before and after mechanical stretching and then after thermally driven shape recovery. Scanning electron microscopy confirms that the Au NPs initially form clusters within the SMP. During stretching, a significant polarization-dependent response develops, where the optical absorbance maximum corresponding to the surface plasmon resonance is redshifted by up to 22 nm and blueshifted by up to 12 nm for polarization parallel and perpendicular to the stretching direction, respectively. This result can be explained by the Poisson effect, where stretching pulls the Au NPs apart and pushes them closer together, parallel and perpendicular to the stretching direction, respectively, resulting in the correspondingly weaker and stronger plasmon coupling. Heating or lack of heating during stretching dramatically affects the recovery process. If the sample is not heated during stretching, the polarization dependence vanishes after shape recovery, while polarization-dependent optical properties remain for samples heated during stretching. Simulations of the polarized optical responses of Au NP dimers at different distances are consistent with experimental results for the clusters of Au NPs in the SMP films and allow estimation of the average interparticle spacings. The finding that the stretching temperature affects the assembly and optical properties after shape recovery implies that the reversibility of the effects of stretching can be controlled and adjusted.

11:30 AM QN08.11.11
Simple One-Pot Synthesis of Au Nanoclusters and the Application in Photothermal Therapy Xujun J. Li; Jie Zhang, Sai Katla and Lei Ma; University of Texas at El Paso, El Paso, Texas, United States.

Remarkable recent advances in Au$_{x}$(SR)$_{y}$ nanoclusters have led to significant applications in catalysis, sensing, and magnetism. However, the existing synthetic routes are complicated such as the use of complex polyacrylamide gel electrophoresis-based nanoparticle separation technique, particularly for the water-soluble Au$_{x}$(SG)$_{y}$ nanoclusters. Here we report a simple one-pot concentration and temperature controlled method for rapid synthesis of the Au$_{x}$(SG)$_{y}$ nanoclusters in as little as 2 h without the need for a low-temperature reaction or even stirring. A systematic time-based investigation was carried out to study the effects of volume, concentration, and temperature on the synthesis of the nanoclusters. This high-temperature method decreases the synthesis time for the nanoclusters by over 10 folds than the currently existing procedures and does not need an inert atmosphere, low temperature (e.g. 0 °C) or stirring, making it an extremely simple and cost-effective process. Furthermore, we, for the first time, discovered that the Au$_{x}$(SG)$_{y}$ nanoclusters exhibit excellent photothermal activities. It was found that 0.75 mg/mL Au$_{x}$(SG)$_{y}$ nanoclusters can achieve 100% cell death for MDA-MB-231 breast cancer cells at a power of 10 W/cm$^2$ of an 808 nm laser source, which demonstrated great potential of Au$_{x}$(SR)$_{y}$ nanoclusters for photothermal therapy.

11:45 AM QN08.11.12
Halide Ions as Morphology Descriptors and Dopants in Colloidal Nanocrystals of Binary Semiconductors and Metal Oxides Sandeep Ghosh; The University of Texas at Austin, Austin, Texas, United States.

Various synthetic handles have been identified over the years, while developing wet chemical protocols for achieving a high level of shape and compositional complexity in colloidal nanomaterials. Halide ions have emerged as one such handle which serve as important surface active species that regulate nanocrystal (NC) growth and concomitant physicochemical properties. Halide ions affect the NC growth kinetics through several means, including selective binding on crystal facets, complexation with the precursors, and oxidative etching. On the other hand, their presence on the surfaces of semiconductor NCs stimulates interesting changes in the intrinsic electronic structure and interparticle communication in the NC solids eventually assembled from them. In this presentation, we will describe these roles of halide ions in the growth of nanocrystals and the physical changes introduced by them.

As a representative example, we will describe a case study wherein pyramid-shaped wurtzite cadmium selenide (CdSe) nanocrystals (NCs) were synthesized by hot injection in the presence of chloride ions as shape-directing agents, which exhibit reversed crystal polarity compared to former reports. Advanced electron microscopy techniques (image-corrected HRTEM with exit wave reconstruction and probe-corrected HAADF-STEM) indicate that the polar [0001] facet constitutes the triangular base of the pyramids while the opposite [0001] facet had been reduced to a tip signifying the merging point for the three lateral facets. Based on a simple model of binding of Cl atoms to surface Cd atoms, Density Functional Theory calculations support the experimental evidence that chloride ions confer higher thermodynamic stability to the (0001) facet over the (0001). This finding of differential relative stability of the two polar facets of wurtzite CdSe is contrary to that of previously reported experiments and calculations on NCs in which no chloride-based additives were deliberately used in the synthesis or no chlorine atoms were considered in the binding models. Self-assembly of these pyramids in a peculiar clover-like geometry, triggered by the addition of oleic acid, suggests that the basal (polar) facet has a density and perhaps type of ligands significantly different from the other three facets, since the pyramids interact with each other exclusively via their lateral facets.

Another relevant case study that will form part of this presentation will include the description of colloidal synthesis of flurine doped indium oxide cubes where fluorine was found to be both a morphology descriptor as well as an aliovalent dopant. Single crystalline 160 nm sized F:In$_{x}$SC$_{3}$ nanoclusters were synthesized using a colloidal heat-up method. The presence of fluorine was found to impart higher stabilization to the (100) facets through density functional theory (DFT) calculations based on a simple model of F-substitution of surface O-sites. These calculations support the experimentally evident cubic morphology resulting from surface binding of F-atoms as confirmed by electron microscopy and X-ray photoelectron spectroscopy (XPS). These cubes exhibit narrow, shape-dependent multimodal LSPR extinction peaks due to corner- and edge-centered modes that are visualized by electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM).

References:
2. Atomically Coherent Attachment of Wurtzite CdSe Nanocrystals—Considerations for Removing Dislocations from Imperfect Attachment Justin Ondry and Paul Alivisatos; University of California, Berkeley, Berkeley, California, United States.

SESSION QN08.12: Nanoparticle Synthesis, Assembly and Applications IV
Session Chairs: Feng Bai and Ying-Bing Jiang
Friday Afternoon, April 26, 2019
PCC North, 100 Level, Room 129 B

1:30 PM QN08.12.01
Colloidal Semiconductor Nanocrystals—Many “Facets” of Halide Ions in the Chemistry of Colloidal Inorganic Nanocrystals—Considerations for Removing Dislocations from Imperfect Attachment Justin Ondry and Paul Alivisatos; University of California, Berkeley, Berkeley, California, United States.
Quantum Confinement Effects on the Photoconductivity of Nanocrystal Thin Films

Reference: X.Y. Li, et al, Nature Photonics, 2018, 12, 159-164

levels. As a new generation of infrared colloidal nanomaterial, their fundamental properties have not been thoroughly investigated to date. This presentation reports the synthesis, new narrow bandgap tetragonal phase, not available in bulk, and contain excess electrons, allowing intraband optical transitions between the first and the second conduction energy obscurant such as fog and mists, making them optimal for use in long-distance thermal sensing and enhanced night vision applications. These quantum dots are synthesized into a with passivating chloride anions. This results in devices with an improved mobility that retain high external quantum efficiencies in the high-injection-current region and also

York University, Brooklyn, New York, United States; 2Department of Electrical and Computer Engineering, New Jersey Institute of Technology, Newark, New Jersey, United States; 3Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, New York, United States; 4Department of Chemical Engineering, Cooper Union, New York, New York, United States.

Colloidal quantum dot-based infrared photodetectors present a promising path toward fabricating sensors and imagers at significantly reduced cost. Herein, we report on recently discovered silver chalcogenide quantum dots that exhibit distinct optical absorption in the mid-wavelength infrared, which is known to have high penetration through airborne obscuring such as fog and mists, making them optimal for use in long-distance thermal sensing and enhanced night vision applications. These quantum dots are synthesized into a new narrow bandgap tetragonal phase, not available in bulk, and contain excess electrons, allowing intraband optical transitions between the first and the second conduction energy levels. As a new generation of infrared colloidal nanomaterial, their fundamental properties have not been thoroughly investigated to date. This presentation reports the synthesis, characterizations, and photoductive photodetector device characteristics and discuss potential impacts that this new nanomaterial could bring to mid-infrared optoelectronics.

Using Light to Manipulate, Assemble and Generate Novel Inorganic Heterostructures in Solution Matthew J. Crane1, Elena P. Pandres2, E. James Davis1, Peter J. Pauzauskie1,2 and Vincent C. Holberg1, 1Chemical Engineering, University of Washington, Seattle, Washington, United States; 2Materials Science and Engineering, University of Washington, Seattle, Washington, United States; 3Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington, United States.

The fabrication of junctions between colloidal nanomaterials has enabled a wide range of technologies, but, as devices approach the single-nanoparticle scale, the rational assembly of nanomaterials remains challenging. In 2018, Arthur Ashkin won the Nobel Prize for developing optical traps, which offer the ability to manipulate individual nanostructures in three dimensions. However, to date, there are relatively limited reports on optical trapping in non-aqueous media, and thus far, nanoscale inorganic materials have only been optically trapped in vacuum and in aqueous solvents. Here, we present several examples of our recent efforts on the use of light to manipulate and generate inorganic heterostructures in non-aqueous solvent systems, including a novel demonstration of the use of optical trapping to manipulate, align, and assemble metal-seeded semiconductor nanowires in organic dispersion, resulting in the fabrication of arbitrarily long heterostructures consisting of periodically repeating, metal-nanocrystal/semiconductor-nanowire junctions. Heat transport calculations and optical images demonstrate that the metal tip of each optically-aligned nanowire undergoes eutectic melting in the optical trap, facilitating the oriented tip-to-tail “nanosoldering” of successive nanowire building blocks. In addition, some of our exciting new results on the large-scale photothermal modification of nanomaterials will also be presented.

Bright Colloidal Quantum Dot Light-Emitting Diodes Enabled by Efficient Chlorination Xiyen Li; University of Toronto, Toronto, Ontario, Canada.

The external quantum efficiencies of state-of-the-art colloidal quantum dot light-emitting diodes (QLEDs) are now approaching the limit set by the out-coupling efficiency. However, the brightness of these devices is constrained by the use of poorly conducting emitting layers, a consequence of the present-day reliance on long-chain organic capping ligands. This presentation will focus on how conductive and passivating halides can be implemented in Zn chalcogenide-shelled colloidal quantum dots to enable high brightness green QLEDs. We use a surface management reagent, thionyl chloride (SOCl2), to chlorinate the carboxylic group of oleic acid and graft the surfaces of the colloidal quantum dots with passivating chlorides anions. This results in devices with an improved mobility that retain high external quantum efficiencies in the high-injection-current region and also feature a reduced turn-on voltage of 2.5 V. The treated QLEDs operate with a brightness of 460,000 cd m2, significantly exceeding that of all previously reported solution-processed LEDs.

Reference: X.Y. Li, et al, Nature Photonics, 2018, 12, 159-164

Quantum Confinement Effects on the Photoconductivity of Nanocrystalline Thin Films James Cassidy and Mikhail Zamkov; Bowling Green State University, Bowling Green, Ohio, United States.

Colloidal quantum dots are size-tunable band gap materials that can be solution processed into thin film optoelectronic devices. However, the device performance is often limited due to the small particle size and inability to effectively transport photoinduced charges via electron hopping or tunneling. Because of this limitation there is a need to understand the effects of both quantum confinement and particle “grain” size contribute to a film’s conductivity. For instance, 15 nm CdSe has been shown to have a 10-fold greater conductance than smaller 4 nm CdSe thin films. Here the effect of particle size offers a more substantial effect than quantum confinement to the conductance of a nanocrystal thin film. However, by employing core/shell materials, such as CdS/CdSe, that exhibit confinement only in the shell we can investigate the effect of quantum confinement independently of grain size. This is done by allowing the CdS core to exceed the Bohr radius, which results in large grain size while allowing the CdSe shell to maintain quantum confinement. By adjusting the dimensions of CdS/CdSe materials even greater thin film photodconductivity, than CdSe of the same size, is achieved by taking advantage of both grain size and quantum confinement effects on photoinduced charge transfer.

Bright and Robust Heavy Metal-Free Quantum Dots Donghyo Hahn1,2, Kooleon Char3 and Wan K. Bae1; 1Seoul National Univ, Seoul, Korea (the Republic of)1, 2Sungkyunkwan University Advanced Institute of NanoTechnology, Suwon, Korea (the Republic of)2.

In this presentation, we provide a synthetic strategy for bright and robust InP based quantum dots (QDs) and their applications to light-emitting diodes. Specifically, we propose a InP emissive core/ZnSeS2, inner shell/ZnS outermost shell heterostructure that consists of environmentally benign, heavy metal-free elements and conduct comprehensive study involving synthesis, spectroscopy and simulation. The systematic study unveils the role of the geometry and composition of proposed heterostructures on the optical bandgap, spectra linewidth and photoluminescence quantum yield (PL QY). In addition, we evaluate the stability of designed QDs on involving thermal stress, oxidation, high energy photon exposure, and the electrical stresses. The highlight of present work is the realization of green and red-emitting QDs exhibiting peak PL emission wave length at 525 and 620 nm
with narrow spectra linewidth (full width at half maximum (FWHM) below 40 nm), PL QY as high as 90 % and prolonged stability against external stresses. Finally we demonstrate QD based light-emitting diodes (QLEDs) that display color-pure green (peak EL = 531 nm, FWHM = 39 nm) and red (peak EL = 637 nm, FWHM = 45 nm) emission and peak external quantum efficiency as high as 3.78 % and 6.2 %, respectively.

3:30 PM QN08.12.07
Surface Engineering to Achieve Water Dispersible Indium Phosphide/Zinc Sulfide Core/Shell Nanocrystals Colin Hessel and Albert J. Wright; Materials Technologies, Physical Sciences Inc, Andover, Massachusetts, United States.

Water dispersibility of photoluminescent semiconductor nanocrystals without a significant drop in photoluminescence quantum yield (QY) is a prerequisite for aqueous applications such as biological labeling or nanocrystal inks. While standard silica coating or ligand exchange phase transfer techniques enable aqueous dispersibility, they often result in low QY (<1%), particle aggregation, or poor scalability. In this contribution, we present a surface engineering approach that enables the phase transfer of aqueous InP/ZnS core/shell nanocrystals with a QY > 35%. Three methodologies were used to transfer as-prepared nanocrystals from the organic to aqueous phases, and each are compared in terms of the resultant aqueous QY, extent of particle aggregation, and scalability. Our approach utilizes the growth of a sacrificial ZnS shell and an optimized exchange ligand that minimize the effects of surface etching that commonly reduces the photoluminescence QY during phase transfer. The scalable approach yields aqueous InP/ZnS nanocrystals that are colloidal stable at room temperature for ~3 months with surface functionality amenable to bioconjugation. Synthetic procedures, analytical characterization, and mechanistic insights will be discussed.

3:45 PM QN08.12.08
Nanoparticle-Based Hollow Microstructures Formed by Two-Stage Nematic Nucleation and Phase Separation Shideh T Rahimnasab, Linda S. Hirst, Amir Keshavarz and Benjamin Stokes; University of California, Merced, Merced, California, United States.

We report a new method to assemble nanoparticle-based hollow microstructures utilizing unusual phase separation kinetics in a two-stage nematic nucleation and growth process. This process generates size-tunable closed-cell foams, spherical shells, and hollow tubular networks composed of closely packed nanoparticles. To assemble these structures we dispersed mesogen-modified nanoparticles in a liquid crystal host at a temperature above the nematic-isotropic transition (TNI). On cooling through TNI we observe the initial segregation of nanoparticles into the shrinking isotropic phase domains. Subsequently, we observed a second stage nucleation of nematic domains inside the nanoparticle-rich isotropic domains, leading to the formation of a variety of hollow structures whose differentiation is controlled by nanoparticle density and cooling rate. Monte Carlo simulations of the initial nucleation stage support experimental observations that initial phase separation controls the number of nanoparticles in each assembly. Microscopy studies suggest that the secondary nucleation step controls the number and size of internal voids. These novel hollow micro-assemblies may find broad applications in controlled release, metamaterials, catalysis, and sensor applications.

4:00 PM QN08.12.09
Strongly Polarized Light Generation from Isotropic Colloidal Quantum Dots Coupled to Fano Resonances Kiyanc Gungor1;2, Onur Erdem1, Burak Guletlik1, Emre Unal1, Mustafa Sak1, Sergey V. Gaponenko1, Shinae Jun2, Eunjoo Jung1 and Hilmi V. Demir2; 1Bilkent University, Ankara, Turkey; 2Los Alamos National Laboratory, Los Alamos, New Mexico, United States; 3National Academy of Sciences, Minsk, Belarus; 4Samsung Advanced Institute of Technology, Yeongtong-gu, Korea (the Republic of).

Semiconductor nanocrystals are highly promising material platforms for use in advanced photonic applications. However, conventional device architectures and fabrication methods cannot exploit their potential. Colloidal quantum dot (QDs) offer high color purity essential to high-quality liquid crystal displays (LCDs), which enables unprecedented levels of color enrichment in LCD-TVs today. [1] However, for LCDs intrinsically requiring polarized backplane illumination in operation, highly polarized light generation using inherently isotropic QDs remains a fundamental challenge to date. To address the need for their effective utilization, we proposed and demonstrated innovative photon management techniques for photonic applications of QDs focusing on polarized color conversion. To achieve polarized color conversion by using isotropic QDs, we studied the plasmonic interaction mechanisms that may modify the density of optical states. Strong dipole orientation dependence of surface plasmon coupled emission is utilized in the in-vacuum processes defined into the v-shaped backlight unit (v-BLU) structure [2] Forward scattering of Fano resonance effectively allowed for polarized light generation that can freely radiate into the farfield. [3,4] Unlike many reports in the literature, our experimentally realized high contrast ratio of 9.70 for red quantum dots is measured at the farfield with a home-made measurement setup similar to LCD operation. To analyze the origin of this polarization response, we investigated the emission kinetics of quantum dots using time resolved fluorescence measurements. Here we observed faster decay rate in the resonating polarization state with higher emission intensity is a direct evidence of the strong modification in density of optical states as a part of Purcell enhancement. [5] In addition, the oriented dipoles of coupled quantum dots to this v-BLU surface is observed using back focal plane imaging. The QDs coupled to v-BLU show a distinct back focal plane pattern, which is only reported for strong dipolar emissions observed in single molecule measurements. [6] In contrast, the unpatterned films of isotropic quantum dots on fused silica and plain gold film show no sign of dipolar emission pattern in their back focal plane images. In the light of measurements unveiling the physics behind the polarized emission mechanism, we finally demonstrated a proof-of-concept display under v-BLU back illumination. Our fabrication includes a special mold fabrication and template stripping steps making the developed v-BLU structure commercially appealing. Also changing the patterning methodology for high yield mass production will be discussed.


4:15 PM QN08.12.10
Fe3+−Cr3+ Nanocubes for Induction Heating Catalysis via Controlled Synthetic Routes Natalia da Silva Moura, Pragathi Durapaneni, Kerry M. Dooley and James A. Dorman; Louisiana State University, Baton Rouge, Louisiana, United States.

Iron catalysts play a vital role in the leading chemicals industry, favoring the production of ammonia, hydrogen, and liquid hydrocarbons through the Haber-Bosch, Water-Gas Shift, and Fischer-Tropsch processes, respectively. These catalysts are beneficial by an increase in surface area, which can be achieved through reduced dimensionality. To produce efficient catalytic performance, uniform temperature routes capable of controlling size and shapes, nanocrystals have been reported, enabling fine tuning of the catalytic properties of a given material. Consequently, for iron oxide (Fe3O4) nanocrystals, for example, structural control also enables improved magnetic properties. In the context of catalysis, Fe3O4 is an interesting material due to its ability to generate localized heat by the conversion of electromagnetic radiation into heat, as seen in magnetic hyperthermia. Therefore, combining the properties of iron catalysts with synthetic control and doping have the potential to make an impact in the chemicals industry.

In this work, thermal decomposition is used to produce monodisperse, cubic shaped, Fe3+−Cr3+O4 nanocubes as a strategy to improve the activity of the iron oxide (Fe3O4) host nanoparticles via Cr3+ doping, while maintaining the magnetic properties of the host lattice. Cr3+ replaces Fe3+ in the octahedral sites of Fe3O4 inverse spinel structure at low doping concentrations (< 15 mol%), and tetrahedral and interstitial sites at higher concentrations. Low Fe3+ and concentration improves activity and redox performance due to coupling of the Fe3+/Fe2+ with Cr3+/Cr4+, and regeneration of Cr4+ on the surface. To confirm this regeneration effect and the site occupancy of Cr in Fe3O4, E-edge X-ray Absorption Spectra of Fe and Cr are collected. The impact of surface Cr4+ on the catalytic efficiency of Fe3+−Cr3+O4 under induction heating catalysis is shown through a butanol condensation/dehydration reaction, and the reaction products are identified via Gas Chromatography-Mass Spectroscopy (GC-MS). The cation regeneration also benefits catalytic performance by increasing the number of active sites, which are measured via CO2 N2 adsorption. In addition, Cr3+ doping changes the pore structure from mesopores to micropores, thereby increasing the surface area, demonstrated through BET measurements. To determine the origin of catalytic enhancement with regards to Cr doping or formation of oxygen vacancies, X-ray Photoelectron Spectroscopy (XPS) is performed to elucidate the local bond environment. Finally, magnetic properties are characterized via Superconducting Quantum Interference Device (SQUID) measurements to show how the saturation magnetization, and coercivity are preserved. Induction heating is characterized by determining the Specific Loss Power of these materials under various magnetic field strengths.

4:30 PM QN08.12.11
Stepwise Seed-Mediated Growth of Self-Registered Anisotropic Plasmonic Nanostructures Ji Feng and Yadong Yin; Chemistry, University of California, Riverside, Riverside, California, United States.

Control over localized surface plasmon resonance frequency of metal nanoparticles by shaping the geometry of the nanostructure has attracted continued attention. In this presentation, we report a stepwise seed-mediated growth method for the synthesis of self-registered anisotropic plasmonic nanostructures. The synthesis relies on using colloidal nanoparticles as substrates for the assembly of the metal seeds, and precise control over the exposure of the metal seeds by surface passivation. The anisotropic seeded growth of metal nanostructure can be induced by creating a physical barrier on the seeds, which partially passivates the exposed area of the seeds. Au dimers, linear trimers and Au-Ag dimers with high purity and distinguishable plasmonic excitation bands have been synthesized. This synthesis method results in rod-like nanostructures perpendicularly registered to the substrates. Taking advantages of this unique feature, we investigated dynamic tuning of the plasmonic excitation of Au-Au and Au-Ag dimers by controlling their orientation relative to the incident light. Such tuning is enabled by switching the substrate to anisotropic magnetic nanoparticles, whose orientation can be magnetically controlled. By tuning the direction of the magnetic field, we show control over the plasmonic resonant modes of the Au-Au dimers and Au-Ag dimers under the incidence of polarized light. The optical switching of Au-Au and Au-Ag dimers exhibits bright colors with high contrast. Finally, we demonstrate the application of such nanostructures as anti-counterfeiting patterns by fixing them in orthogonal orientations in a hydrogel film.

4:45 PM QN08.12.12
Fabrication of Large-Area Arrays of Vertically Aligned Gold Nanorods Wenbo Wei1, Feng Bai2 and Hongyou Fan2; 1Henan University, Kaifeng, China; 2Sandia National Laboratories, Albuquerque, New Mexico, United States.

Anisotropic nanoparticles, such as nanorods and nanoprisms, enable packing of complex nanoparticle structures with different symmetry and assembly orientation, which result in unique functions. Despite previous extensive efforts, formation of large areas of oriented or aligned nanoparticle structures still remains a great challenge. Here, we report fabrication of large-area arrays of vertically aligned gold nanorods (GNR) through a controlled evaporation deposition process. We began with a homogeneous suspension of GNR and surfactants prepared in water. During drop casting on silicon substrates, evaporation of water progressively enriched the concentrations of the GNR suspension, which induces the balance between electrostatic interactions and entropically driven depletion attraction in the evaporating solution to produce large-area arrays of self-assembled GNR on the substrates. Electron microscopy characterizations revealed the formation of layers of vertically aligned GNR arrays that consisted of hexagonally close-packed GNR in each layer. Benefiting from the closepacked GNR arrays and their smooth topography, the GNR arrays exhibited a surface-enhanced Raman scattering (SERS) signal for molecular detection at a concentration as low as 10^−13 M. Because of the uniformity in large area, the GNR arrays exhibited exceptional detecting reproducibility and operability. This method is scalable and cost-effective and could lead to diverse packing structures and functions by variation of guest nanoparticles in the suspensions.

SYMPOSIUM SM01

Materials for Biological and Medical Applications
April 22 - April 26, 2019

Symposium Organizers
Wonmo Kang, Naval Research Laboratory
Laura Na Liu, University of Heidelberg
Jwa-Min Nam, Seoul National University
Seila Selimovic, National Institutes of Health

* Invited Paper

SESSION SM01.01: Materials for Biological and Medical Applications I
Session Chairs: Wonmo Kang and Marc Raphael
Monday Afternoon, April 22, 2019
PCC North, 200 Level, Room 229 A

1:30 PM SM01.01.01
Multivalent Glycosylated Nanoparticles for Specific Binding and Killing of Bacteria Shuai Hou and Hongwei Duan; Nanyang Technological University, Singapore, Singapore.

Carbohydrate-protein recognition plays a key role in cell-cell and host-pathogen interactions, stimulating widespread interest in developing multivalent glycoconjugates with superior binding affinity for biological and medical uses. We have developed a class of glycosylated plasmonic nanoparticles to specifically target the lectins expressed on the surface of bacteria and realize the near-complete killing of the bacteria with laser irradiation.

We first explored the use of Raman-encoded silver-coated gold nanorods (Au@Ag NRs) as scaffolds to form multivalent glycoconjugates. The plasmonic scaffolds afford high-loading of the mannoside clusters, and their optical properties offer the possibilities of monitoring and quantitative analysis of nanoparticle–bacteria recognition. Using E. coli strains with tailored on/off of the FimH receptors, we have demonstrated that Raman-encoded NRs not only allow for real-time imaging and spectroscopic detection of specific binding of the glycan-NR conjugate to the bacteria, but also enable efficient photothermal conversion of Au@Ag NRs in the near-infrared spectral window to realize eradication of the bacteria. Further work used galactosylated copper sulfide nanocrystals (Cu2S NCs) to target Pseudomonas aeruginosa via galactose-LecA interactions. Cu2S NCs show strong surface plasmon resonance in the second near-infrared (NIR-II) window and enable simultaneous photothermal and photodynamic therapies. We observed excellent specificity of the galactosylated Cu2S NCs towards LecA with a LecA-deficient P. aeruginosa strain as the control group. We then used a 1064-nm laser to kill the bacteria and assessed the contribution of photothermal and photodynamic processes.

These results establish that glycosylated nanoparticles, which integrate the recognition capability of carbohydrates and the therapeutic function of nanoparticles, are an effective platform for the targeted killing of bacteria. We also envision that optically-active plasmonic glycoconjugates hold great potential for screening multivalent glycan ligands for therapeutic and diagnostic applications.

1:45 PM SM01.01.02
Multi-Color Electron Microscopy of Cellular Ultrastructure Benjamin Bammes1, Ranjan Ramachandra2, Robert Bilhorn1 and Mark Ellisman2; 1Direct Electron, LP, San Diego, California, United States; 2National Center for Microscopy and Imaging Research, University of California, San Diego, La Jolla, California, United States.

Transmission electron microscopy (TEM) is the primary method to image biological cellular ultrastructure, though it is not possible with conventional TEM to label and distinguish different kinds of molecules in a single image. This serious limitation was recently addressed through the development of “multi-color EM,” which uses selective lanthanide ion tagging and electron energy-loss filtered imaging (Ramachandra et al., 2014, Microsc Microanal. 20; Adams et al., 2016, Cell Chem Biol. 23) yielding data
analogous to multi-color fluorescence microscopy but at ~100x the magnification. While this technique promises to reveal novel structural information, it is tedious (requiring multiple long exposures with different energy filter settings), terribly inefficient (depending on the small fraction (<1%) of primary TEM electrons that are inelastically scattered), and yields noisy images with significantly lower resolution than is achievable by TEM imaging.

To improve the throughput, efficiency, and resolution of multi-color EM, we have developed a new multi-color EM technique with 4D-STEM, which uses a high-speed pixeleted detector to record the vast majority of the primary electrons that interact with the specimen.

In order to achieve the necessary sensitivity for this technique, the pixeleted detector must deliver synchronized (global shutter) readout of a large number of pixels (at least 512 × 512 pixels) and it must have single-electron sensitivity for electron counting.

We used the DE-16 direct detection camera in conjunction with the DE-FreeScan scan generator (Direct Electron LP, San Diego, CA USA) to collect a 4D-STEM dataset of a cellular mitomatrix sample, with mitochondria labeled by cerium and containing gold nanoparticles. After correcting for distortions in the defraction patterns, we were able to develop a metric to distinguish the cerium labels and gold nanoparticles, while simultaneously generating bright-field and dark-field images of the specimen at significantly higher resolution than is possible through fluorescence light microscopy.

2:00 PM SM01.01.03
Fabrication and Characterization of Biodegradable Metal Based Microelectrodes for In Vivo Neural Recording Chaoxing Zhang1,2, Teresa Wen1, Khaleed Razak1,4, Jiajia Lin1,2, Edgar Villafana2, Hector Jimenez2 and Huinan Liu1,2,3; 1Materials Science and Engineering, University of California, Riverside, Riverside, California, United States; 2Department of Biomedical Engineering, University of California, Riverside, Riverside, California, United States; 3Biomedical Sciences Program, School of Medicine; Stem Cell Center, University of California, Riverside, Riverside, California, United States; 4Neuroscience Graduate Program, University of California, Riverside, Riverside, California, United States; Psychology Department, University of California, Riverside, Riverside, California, United States.

Neural electrodes have been widely used to monitor neural signals and/or deliver electrical stimulation in the brain. Currently, biodegradable and biocompatible materials have been actively investigated to create temporary electrodes that could degrade after serving their functions for neural recording and stimulation from days to months. The new class of biodegradable electrodes eliminate the necessity of secondary surgery for electrode removal. In this study, we created biodegradable, biocompatible, and implantable magnesium (Mg)-based microelectrodes for in vivo neural recording for the first time. Specifically, conductive poly-3,4-ethylenedioxythiophene (PEDOT) was first deposited onto Mg micro/meso substrates by electrochemical deposition, and a biodegradable insulating polymer was subsequently sprayed onto the surface of electrodes. The tip of electrodes was designed to be conductive for neural recording and stimulation, while the rest of electrodes was insulated with a polymer that is biocompatible with neural tissue. The charge storage capacity and impedance of Mg-based microelectrodes and their performance during neural recording in the auditory cortex of a mouse were studied. The results first demonstrated the capability of Mg-based microelectrodes for in vivo recording of multi-unit stimulus-activated activity and spontaneous activity in the brain.

2:15 PM SM01.01.04
A Sneak Peek into the Material Science of Active Pharmaceutical Ingredients—The Importance of Solid-State Characterization in Drug Development Paroma Chakravarty; Small Molecule Pharmaceutical Sciences, Genentech Inc., South San Francisco, California, United States.

Small organic molecules exhibiting therapeutic properties are known as active pharmaceutical ingredients (API) and are of great interest in pharmaceutical material science. These API can exist in several crystalline forms as well as in different states of disorder of which the amorphous form is of great interest due to their greater free energy which results in higher bioavailability and exposure in vivo. Detailed screening as well as subsequent characterization of the different forms with varying degrees of crystallinity is imperative to choosing a suitable lead candidate that will elicit the required therapeutic response in vivo. Thus the material science aspect of drug development plays a vital role in the pharmaceutical industry since it is responsible for proper physical form selection and its maintenance in the formulation during its shelf life. Polymorphism, amorphization or changes to chemical composition are several ways in which the physical form of the API may be altered which may bring about a change in its pharmaceutical properties and ultimately affect the final drug product and its performance. This talk focuses on the material science part of pharmaceutical drug development and tackles the different challenges faced in characterizing drug substances in both the discovery and development stage as well as in the formulation. Judicious form screening as a salt or polymorph, form changes during processing and unit operations and vitrification of crystalline materials for improving bioavailability will be covered as well as analytical techniques used for such characterization. The focus is on several case studies involving both drug substance and drug product with emphasis on experimental (X-ray diffraction, spectroscopy, microscopy, thermal analysis) and computational characterization techniques to showcase advances in pharmaceutical material science encompassing both ordered and disordered materials.

2:30 PM SM01.05.01
Density Control and Patterning of Biosensor Surfaces Using Modified Poly-L-Lysine Polymers Jacopo Movilli1, Daniele Di Iorio1, Andrea Rozzi2, Roberto Corradini2 and Jurriaan Huskens1; 1Molecular NanoFabrication group, University of Twente, Enschede, Netherlands; 2Department of Chemistry, University of Parma, Parma, Italy.

Biosensors and materials for biomedical applications generally require precise chemical functionalization to bestow their surfaces with desired properties, such as specific molecular recognition and antifoiling properties. Consequently, tailoring the chemistry at the biosensing interface has a crucial role in obtaining the best selectivity and sensitivity. Especially for DNA biosensors, either biological or artificial probes, as well as antifoiling moieties, need a defined type of chemistry to be anchored with respect to their chemical modification and the type of substrate, affecting the biodistribution. In addition, control of the surface probe density is required for achieving high sensitivity.

Traditional methods have the applicability limited to specific substrates and aim to control the density at the surface modification step, with the drawback of having to test the hybridization efficiency every time. Recently, polyelectrolytes were used in biosensing to tailor the probe type and distribution. Furthermore, the ensemble of substrates for biosensing purpose has been increased thanks to the multiple nature of polymers and their electrostatic interactions. The chemi/physi sorption of modified polyelectrolytes provides advantages for the immobilization of biomolecules and for biosensing applications. At physiological pH, poly(L-lysine) (PLL) polymers readily and strongly adsorb onto a variety of metal oxide surfaces through multivalent electrostatic interactions between the positively charged lysine side-chains and a negatively charged surface. As a result, PLL polymers, which are easy to functionalize thanks to the amino groups in the side chain, allow the accommodation of the grafted functional moieties over the substrate, maintaining their adsorption properties. Based on this approach, biorecognition surfaces were prepared by deposition of modified PLL polymers grafted with various fractions of oligo(ethylene glycol) (OEG, antifoiling) and maleimide (Mal) moieties (PLL-OEG-Mal), so that both the type of functionalization and the control over the density is achieved at the same time, during the synthetic step, verified by 1H-NMR. PLL-OEG-Mal polymers were self-assembled at the substrate and coupled to thiol-peptide nucleic acid (PNA) probes, forming a real-time DNA biosensor. A linear relationship between the probe density and the PLL grafting density was found monitoring the frequency shift of the hybridization step for the complementary DNA versus probes per % of grafted Mal, thus confirming the validity of the density control in the synthetic PLL modification step without the need of further surface characterization. Thanks to their advantages, modified PLL polymers can be used to tune the surface properties, accommodating several clickable side groups as linkers and antifoiling moieties, and forming different architectures as layer-by-layer and μ-arrays, as well as their application in soft lithography and pillar structures.

References:
The oral cavity harbors a wide array of microbiota which if perturbed, would result in the loss of mutualistic/symbiotic balance leading to diseases. The aggregates of these microorganisms can orderly lay in a protective sheath coined as extracellular polymeric substance (EPS), to form oral biofilm a.k.a. dental plaque. There is mounting evidence that the dental biofilm can be the culprit of several diseases such as dental caries which affects 2.4 billion people worldwide.

In the biofilm, the biofilm itself is induced by the presence of carbohydrates causes organic acids production (p4–4.8) demineralizing the tooth enamel. The most common serious pathogen involved in the dental biofilm is the gram-positive bacteria, streptococcus mutans (S. mutans), which actively produces EPS and acids.

Unfortunately, the rigorous solution to the dental caries is compounded due to the multifactorial nature of the disease. Nanoparticles (NPs) can offer an unequivocal solution to the biofilm issue with the privilege of multifunctionality, on-demand controlled release of drugs, high loading efficiency, selectivity, and trackability. Importantly, the nanoparticles can be designed to be ‘self-contained’ and exert the therapeutic effects without the utilization of conventional antibiotics. Nevertheless, as a major group of nanobiotics, the experimentation with metallic nanoparticles has raised concerns regarding their accumulation and non-degradation.

Carbon dots (CDots) are the emergent class of carbon family which have attracted a host of research in recent years due to the ease of fabrication, tunable luminescent properties, and the abundance of functional groups. These properties combined with their degradability offer a unique platform for combating bacteria. Herein, we present for the first time, a ‘particle in particle’ approach for targeting the EPS with its characteristic pH to release the load of inherently therapeutic CDots to kill notorious S. mutans. Specifically, phosphonium containing CDots have been wrapped in a layer of poly(styrene)-b-poly(n-dimethylocthio methacrylate) (PS-b-PDMA) which shows pH responsiveness upon encountering acidic pH. Moreover, phosphonium ions have been utilized to confer antibacterial properties to the NPs as with more pronounced to varying pH compared to their ammonium counterparts (pKa 1.8 vs 9.3).

The retained load of therapeutic CDots will get liberated only when in touch with the pH of EPS. This approach would not only lead to the biofilm dispersal and enhanced the bacterial susceptibility but would also exert the antibacterial properties in situ without any external drugs. Moreover, the absence of any external stimuli, for example, H2O2 and photostimulation, is a boon which reduces the unintentional toxicity.

We have demonstrated that these NPs could suppress the biofilm EPS and decrease the S. mutans viability in the in vitro human tooth model of the biofilm. The mechanism of action can be classified as ROS generation and fragmentation of genomic DNA on the subcellular level. We have shown, in vivo, in the rat model of dental biofilm that these nanoparticles could successfully decrease the cultivable S mutants within 13 days using the plate count assay and S. mutans detection kit. It has been recognized through histopathological examination that these NPs did not interfere with the normal activities of the major organs while the dental caries scoring indicated a decrease in the caries development. The gene expression profiling of the oral microbiota from rats revealed that the change in the microbiome diversity was not statistically significant among groups. Therefore, our approach has great implication for the application of nanomaterials as degradable antibiofilm in the dental clinic.

3:00 PM BREAK

3:30 PM SM01.01.07

Self-Sterilizing Photodynamic Polymers for Anti-Infective Materials

Bharadwaja Sriram Tirumala Peddinti; North Carolina State University, Raleigh, North Carolina, United States.

Increase of antibiotic resistance in pathogens has directly impacted healthcare industry. With only a few novel discoveries in the field of antibiotics since last two decades, often referred to as the discovery void, drug discoveries in pathogens has increased. Previously, infections that were easily treatable have now become fatal. Infections caused by antibiotic-resistant pathogens can occur anywhere, but, it is observed to take maximum effect in healthcare settings such as hospitals and nursing homes. The pathogens adhere to surfaces such as linens, counter tops, drains and equipment, medical sanitary ware and so on. Moreover, patients in hospitals are easily affected due to decreased immunity.

According to a report by Center for Disease Control and Prevention (CDC), 1 out of every 20 hospital patients is affected by nosocomial infections subsequently resulting in 100000 deaths in the United States of America. Out of these, 23000 deaths on an average are attributed to drug-resistant pathogens such as methicillin resistant Staphylococcus aureus and vancomycin-resistant Enterococcus faecium. In addition to this, $9.8 billion are invested in treatment of such infections. The conventional routes of treatments are proving to be inconsequential and a major part of tackling such uses is antibiotic. But, with the increase in drug-resistant strains it is only a matter of time when all the treatment methods fail. Although several methods such as chemical disinfectants, ionizing radiation, ultra-violet treatments are used in addition to antibiotics but, they are not effective due to various reasons. Chemical disinfectants and ionizing radiation are not FDA approved. Moreover, radiation techniques are cost intensive and ultra-violet radiation is harmful to healthy cells. So, alternative techniques must be investigated that can be utilized to prevent the loss due to hospital acquired infections (HAIs). Consequently, alternative techniques for surface disinfection must be investigated for their application as preventive techniques instead of looking for a cure. One such method that has recently come into light in the last two decades is photodynamic therapy (PDT).

Commercial photosensitizers (PSs) such as Photofrin and Protoporphyrin IX have been used in Photodynamic therapy (PDT) for treating initial stages of skin cancer, acne, and psoriasis. It involves three components: a photosensitizer, a visible light source and cytotoxic singlet oxygen. Initially, the PS is applied to the area affected by the cancer cells. After the PS is absorbed into the cells, the target area is illuminated by red colored light, thus, activating the PS. Activated PS can exchange energy with oxygen that diffuses through the cells, converting it into singlet oxygen ($^{1}{O_{2}}$). Being highly energetic readily reacts with various components in the cell, ultimately leading to cell death. The idea of this study is to incorporate such photosensitizers into polymeric matrices that can be applied as surfaces that provide non-specific preventive measures, rather than as specific cures.

In this study, 1% (w/w)ZnTMPyP of porphyrin class has been physically incorporated in an Olefinic Block Copolymer (OBC) via melt-pressing. Inactivation studies were performed on four bacterial strains (two Gram-positive and three Gram-negative at various illumination intensities). Furthermore, time based illumination studies were conducted at various illumination intensities with Staphylococcus aureus (5–80 mW/cm², 5–60 min illumination time). Both the gram-positive bacteria showed ~6 log units reduction (~99.999% killing) at the end of 60 minutes whereas all the three gram-negative bacteria showed at least ~3 log units reduction (~99.9% killing). Antiviral efficacy of films was determined against Vesicular stomatitis virus (VSV) (~99.999 % inactivation). Human adenovirus-5 (~99.956% inactivation) and Influenza A virus (~99.950 % inactivation).

3:45 PM SM01.01.08

Communication—Metabolites-Enhanced Antibacterial Activity of Self-Assembled Nano-Peptide Amphiphiles for Treating Antibiotic Resistant Bacteria

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Numerous bacterial stains have become resistant to conventional antibiotics in recent years. Fortunately, an increasing body of research indicates that through the addition of specific metabolites (like sugars), the antibacterial activity of self-assembled nano-peptide amphiphile (SANPAs) has been designed in this study to treat antibiotic resistant bacterial infections and to reduce the use of antibiotics. Here, SANPAs were self-assembled into nanorod structures with a nanoscale diameter at concentrations greater than the critical micelle concentration (CMC). Both Gram-positive and Gram-negative bacteria were treated with SANPAs with metabolites supplementation. After various amounts of time metabolites pre-incubation, SANPAs reduced bacteria growth relative to non-metabolite treatments at all concentrations. Cytotoxicity studies showed that the presence of metabolites seemed to slightly ameliorate the cytotoxic effect of the treatment on model human fetal osteoblasts (bone forming cells) and human dermal fibroblasts. In conclusion, we demonstrated here that SANPAs-like nanomaterials have a promising potential to treat antibiotic resistant bacteria especially when added to metabolites, potentially limiting their associated infections. By comparison of SANPAs treatments under different communication conditions, the results further provide resource for researcher to design novel agents and treatment methods against antibiotic resistant bacterial infection.

4:00 PM SM01.01.09

Novel Polymeric Heart Valves Using Low-Fouling PEGDA and Fiber Composites

Xing Zhang, Feng Guo, Chang Liu, Yun Bai and Rui Yang; Chinese Academy of Sciences, Shenyang, China.

Heart valve disease with major symptoms of stenosis and regurgitation is prevalent worldwide. Surgical replacement of diseased heart valves at the end-stages has been widely performed with mechanical valves (MVs) or bioprosthetic heart valves (BHV).s. All these current devices have significant limitations with risks of further morbidity and mortality. For example, MV’s may cause hemorrhage and thromboembolism, and require anticoagulation for the lifetime of the patients. BHVs show better hemodynamic behavior due to the composition and structural similarity to native heart valves when compared to MVs, however, they do show limited durability because of calcification and progressive degeneration [1]. Thus, polymeric heart valve (PHV) prostheses combining the advantages of MVs and BHVs with long-term durability and no necessity for permanent anticoagulation are of great interest and also show potential applications in advanced transcatherter devices.

In this study, two types of silk fibroin (SF) fiber membranes with anisotropic (ASF) and isotropic (ISF) properties were prepared by electrospinning methods, and were further combined with poly(ethylene glycol) diacrylate (PEGDA) hydrogels to serve as polymeric heart valve (PHV) substitutes (PEGDA-ASF and PEGDA-ISF). The uniaxial tensile...
tests showed obvious anisotropy of PEGDA-ASF composites with elastic moduli of 10.95 ± 0.19 MPa and 3.55 ± 0.32 MPa, respectively, along the direction parallel and perpendicular to the fiber alignment, close to those of native aortic valve leaflets, while PEGDA-ISF processed isotropic property with elastic moduli of 4.54 ± 0.43 MPa. These novel PHVs consisted of polymeric fibers to mimic the fibrous networks in the fibrosa and ventricularis layers for stress bearing, as well as PEGDA hydrogels to improve anti-fouling function [2,3]. Furthermore, the presence of PEGDA hydrogels in the composites improved the resistance to progressive calcification of the embedded fibers in vitro, likely due to prevention of large-size hydrated ions to pass through by the polymeric networks of the hydrogels [3]. The non-fouling PEGDA hydrogels encapsulated the surfaces of the composites and prevented contact between platelets and the underlying fibers [4]. Pulse duplicator tests presented good hydraulic performance characteristics of these PHVs from PEGDA-ASF and PEGDA-ISF composites according to the ISO 5840-3 standard. Finite element analysis (FEA) revealed the PEGD-ISF valve with anisotropic property showed a lower peak maximum principle stress value (2.20 MPa) in commissures during diastole compared to that from the isotropic PEGD-ISF valve (2.37 MPa). In systole, the bending area of the PEGD-ISF valve was close to free edges, however, which appeared in the belly portion and near the attachment line for the PEGD-ISF valve. Hence, our results revealed that anisotropic properties played important roles not only in mechanical properties, but also in hydraulic performance of these artificial PHVs. These novel PHVs with good biocompatibility and hemodynamic property can likely be used for heart valve replacement in future.

References
Recent advances in molecular biology, single cell manipulation and data analysis techniques have allowed us to look into the molecular states of individual cells with unprecedented detail. These methods have made it possible to investigate how the genotype in combination with internal and external regulatory factors guide the development of complex and diverse phenotype. However, these methods rely on cell lysis and can provide only a snapshot of the cellular state. This makes it challenging to monitor gene expression changes over time. Inferences about dynamic cellular processes are obtained by constructing pseudo-time trajectories from the continuum of molecular states present in a cell population that can reflect the essence of a single cell trajectory. However, the dynamics of cell state may be non-hierarchical or stochastic which the computational algorithms cannot always capture. In order to acquire a holistic understanding of decision-making pathways involved in processes such as cell reprogramming, differentiation and maturation, tracking the same cell in time is necessary. Our long-term goal is to develop a single-cell microfluidics platform that can temporally examine cells by performing precise cellular manipulations (e.g. genetic editing using CRISPR/Cas9) and subsequent analysis of internal cellular biomarkers in a non-destructive manner. Such a system would allow us to monitor the biochemical changes in cells over time and correlate these to the external inputs and perturbations.

Localized electroporation has emerged as an effective technique for introducing the desired changes in cellular systems by delivering foreign molecules such as nucleic acids. Unlike bulk electroporation where the entire cell membrane is exposed to a strong and non-homogeneous electric field, localized electroporation utilized nanostructures (such as nanochannels) to confine the electric field to only a fraction of the plasma membrane. This controlled perturbation allows for efficient transport of molecules into the cells as well as helps maintain high cell viability. As such, localized electroporation is also being used to address the converse problem, i.e. to non-destructively sample the cytosolic contents of living cells.

Although several experimental reports demonstrate the phenomena of localized electroporation, a mechanistic understanding of the different parameters involved in the process is lacking. In this work, we present a multiphysics model that 1) estimates the transmembrane potential developed across the cell membrane in response to a localized electric field, 2) predicts the electro-pore distribution in response to the local transmembrane potential drop and 3) calculates the molecular transport into and out of the cell based on the predicted pore-sizes. Using the model, we identify that cell membrane tension plays a crucial role in enhancing both the amount and the uniformity of molecular transport, particularly for large proteins and plasmids. We also find that a critical voltage range is necessary for efficient electroporation. We qualitatively validate the model predictions by delivering large molecules (fluorescent-tagged bovine serum albumin and mCherry encoding plasmid) and by extracting an exogenous protein (tdTomato) in an engineered cell line on a localized electroporation platform. The findings presented here should inform the future design of microfluidic devices for localized electroporation based sampling and temporal, single cell analysis. Eventually, high throughput temporal analysis of single cells would help us gain insights into fundamental aspects of developmental biology, study the progression of diseases such as Alzheimer’s and Parkinson’s and evaluate the efficacy of drugs over time.

Dissolved oxygen [DO] is crucial to environment, industry, life technology, and human health, etc. Hypoxia[1] (e.g. genetic editing using CRISPR/Cas9) and subsequent analysis of internal cellular biomarkers in a non-destructive manner. Such a system would lead to a breakthrough in wound healing therapy. However, the underlying mechanisms within the cells during electrotaxis remain still unclear.

Endogenous electrical fields play a major role in various biological processes from embryonic development to cell division and migration (electrotaxis). The latter has been extensively researched due to its involvement in wound healing processes. A better understanding of electrotaxis induced by external electrical fields (direct current), could hence lead to a breakthrough in wound healing therapy. However, the underlying mechanisms within the cells during electrotaxis remain still unclear.

The main limitation for research, as well as the clinical application of direct current therapy for directed cell migration, lies within the utilized electrodes. Metal electrodes made of platinum or copper, as well as silver chloride, corrode and release toxic by-products under direct currents, which are harmful to cells and in addition, might influence their migratory function. Therefore, all electrotaxis experiments until now require agar salt bridges to connect the electrodes to the cell chamber, which lead to a bulky and inefficient experimental setup. A better solution for the stimulation material could improve cellular research and facilitate the transition towards clinical use. As an alternative, we propose the use of polyimide-based iridium oxide electrodes coated with poly(3,4-ethylenedioxythiophene) poly styrene sulfonate (PEDOT:PSS). These electrodes are able to maintain stable ionic currents over long periods of time and can drive electromigration of cells without the release of any cytotoxic by-products. Using a simple electrotactic chip we were able to show that PEDOT/PSS electrodes have sufficient ion filling capacity to drive electromigration of skin cells in an agar bridge free system. The chip was fabricated through soft lithography of polydimethylsiloxane (PDMS) which was chemically bonded to a glass coverslip through surface modification with oxygen plasma. The chamber consists of a channel with a seeding area for the cells and two reservoirs at both ends of the channel for medium and the insertion of the electrodes. The use of polyimide-based electrodes allows the reusability of these for several experiments, facilitates the assembly of the electrotactic chamber and greatly reduces the associated cost.

During the experiments, a constant voltage was applied to the electrodes and the current was continuously monitored. Time-lapse photography documented the directed migration and the cell motility was quantified utilizing circular statistics. It was found that pre-oxidation/reduction of the PEDOT/PSS electrodes increased the current injection and subsequently the possible charge delivery to the cells. We conclude that PEDOT based electrodes can be efficiently used for direct current stimulation and have the power to influence the migration of cells relevant to the healing of human skin. The combination of polyimide-based reusable electrodes and disposable microfluidics make a cost-efficient analysis of electrotaxis possible at high throughput.

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (grant agreement No. 759655).

New Oxygen Sensor for In Vivo Dissolved Oxygen Sensing and In Vivo Hypoxia Imaging Jiaze Li, Yuan Qiao, Tingting Pan, Ke Zhong, Jiaxing Wen, Fengyu Su and Yanqing Tian; 1Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen, China; 2SUSTech Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen, China.

Dissolved oxygen [DO] is crucial to environment, industry, life technology, and human health, etc. Hypoxia[1] (≤0.5% O2, usually at tumor environments) is relevant to cancer, stroke, arteriosclerosis, Parkinsonism, and Alzheimer's disease etc.. Therefore, in vivo dissolved oxygen detection is essential for disease prevention and treatment. For dissolved oxygen detection, phosphorescence based optical oxygen analysis showed superior performance among several ways with noninvasive sensing, no oxygen consumption, high sensitivity, fast responses and single cell scale sensing. Herein, five kinds of multi-arm block copolymers were synthesized by atom transfer radical polymerization (ATRP) to load the excellent hydrophobic oxygen probe platinum (II)-5,10,15,20-tetrakis-[2,3,4,5,6-pentafluorophenyl]-porphyrin (PtTFPP) for optimizing PtTFPP's performance in hypoxia sensing and imaging. Among them, fluoropolymers were introduced with their excellent capacity to dissolve and carry oxygen for investigating carriers' structure-property relationship. Under nitrogen atmosphere, high quantum efficiency of PtTFPP in fluorine-containing micelles could reach to 22% without complicated modification of PtTFPP. Oxygen-nitrogen titration by a gas manipulator showed that fluorine-containing micelles have higher oxygen sensitivity (I0/I1) than fluorine-free ones, and micellar sensors are more sensitive under body temperature (37°C) than room temperature.
The sensors reported here might be capable for at least 10 minutes without obvious decay, indicating that the PtTFPP possessed excellent in vivo stability and strong phosphorescence signal after being encapsulated by our materials. Thus, the phosphorescence image at tumor region is much brighter, and the phosphorescence intensity at tumor region is 1.6 times higher than that of normal region. Moreover, the phosphorescence imaging lasted for at least 10 minutes without obvious decay, indicating that the PtTFPP possessed excellent in vivo stability and strong phosphorescence signal after being encapsulated by our materials. Therefore, the long-term efficacy may be jeopardized and the constant electrical stimulation may trigger compensation mechanisms. Power supply is also an issue for this type of implanted electronic devices.

Session SM01.03: Materials for Biological and Medical Applications III

Materials and Devices for Transient Electronic Implants

This talk summarizes concepts in materials science that serve as the basis for transient electronic implants, as a new paradigm for treating injuries and tracking recovery. Here, engineered device platforms provide monitoring and/or therapeutic functionality during the time course of a natural biological process such as healing, and then disappear into the body, without a trace, through mechanisms of bioreorption. This mode of operation eliminates unnecessary device load on the body, and associated risk to the patient, in a way that bypasses the need for secondary surgical extraction. Examples of biodegradable materials and device designs will be presented in the context of (1) electrical stimulators for accelerated neuroregeneration in damaged peripheral nerves, (2) cardiac pacemakers for recovery from heart surgery and (3) programmable drug release vehicles for treatment of disease.

TiO2 nanotube arrays constitute highly versatile scaffolds that are suited for long-term organotypic culture of neuronal tissue, including retina explants and beyond. While tube diameter and surface roughness [1] are central parameters for successful culture and have to be optimized for every specific tissue type, super hydrophilicity ensures nutrition supply by a wetting layer of culture medium even in absence of complicated perfusion systems [2]. Clearly adhesion between tissue explants and nanotube scaffolds plays a key role for maintaining tissue integrity. Lift-off approaches are, on the other hand, desirable for tissue transfer and nanotube regeneration, respectively. Employing extensive environmental scanning electron microscopy (ESEM) as well as laser scanning microscopy (LSM) studies we address both aspects and demonstrate that UV-light exposure and enzymatic treatment are ideally suitable for nanotube regeneration. Based on these findings, we present an assay for concurrent biomechanical straining and in situ imaging employing ESEM and LSM. Thus, we will be able to find correlations between structural components of retina and their variation in tissue mechanics. This will pave the way for in vitro studies on tissue regeneration and surgery techniques in combination with drug testing.

References:

1:30 PM SM01.03.02 Effective Weight Control via an Implanted Self-Powered Vagus Nerve Stimulation Device

Obesity is a global health issue that is suffered by over 700 million people worldwide.[1] Common approaches for treating obesity include non-surgical (excise) and surgical (invasive) treatments, which normally have a high potential of weight rebound or can introduce serious complications.[2] Recent studies demonstrated that vagus nerve blocking and stimulation have multiple physiologic functions related to food intake, energy metabolism, and glycemic control, which can result in a meaningful weight loss. Nevertheless, like many other electrical nerve stimulation therapies, the electrical signals and corresponding biological activities are very hard to be correlated, particularly for such irregular food taking and stomach peristaltic activities. Therefore, the long-term efficacy may be jeopardized and the constant electrical stimulation may trigger compensation mechanisms.[3] Power supply is also an issue for this type of implanted electronic devices.

Here we present an implanted vagus nerve stimulation (VNS) system that is battery-free and spontaneously responsive to stomach movement. The VNS system comprises a flexible and biocompatible nanogenerator that is attached on the surface of stomach. It generates biphasic electric pulses in response to the peristalsis of stomach. The simulated satiety signals deceive the brain via vagal afferent fibres,[4] and reduces food intake when the stomach is in motion. This strategy was successfully demonstrated on rat models. Within 100 days, the average body weight was controlled at 350 g, 38% less than the control groups. This new VNS system correlated nerve stimulation with targeted organ functionality through a smart, self-responsive device, and demonstrated an outstanding weight control capability better than other electric stimulation strategies. This work also provides a new concept in therapeutic technology using artificial nerve signal generated from coordinated body activities.

References:

11:45 AM SM01.02.05 Non-Swellable, Cytocompatible Hydrogels with Enhanced Stiffness and Toughness

Human skin exhibits high stiffness of up to 100 MPa and high toughness of up to 3,600 J m⁻² despite its high water content of 40–70 wt%. Engineering hydrogels have rarely possessed both high stiffness and toughness, because compliant hydrogels usually become brittle when excess crosslinker is added to make the gel stiff. Furthermore, conventional hydrogels usually swell under physiological conditions, weakening their mechanical properties. Here, we designed a non-swellable hydrogel with high stiffness and toughness by interpenetrating covalently and ionically crosslinked networks. The stiffness is enhanced by utilizing ionic crosslinking sites fully, and the toughness is enhanced by adopting synergistic effects between energy-dissipation by ionic networks and crack-bridging by covalent networks. Non-swelling behaviors of the gel are achieved by densifying covalent and ionic crosslinks. The hybrid gel shows high elastic moduli (up to 108 MPa) and high fracture energies (up to 8,850 J m⁻²). In vitro and in vivo swelling tests prove non-swelling behaviors of the gel. Live/dead assays show 99% cell viability over a period of 60 days.

References:
The study of the restoration of vision is one of the most popular research topics in neuroscience and biomedical sciences. A functional/adaptive retinal prosthesis is highly sought after to combat degenerative eye diseases and build foundational devices for future engineering models. A sub-retinal device requires a specific structure compared to other prosthetics. However, the specifics of this work also require high transparency as a performance metric. Low impedance and high Charge Injection Capacity (CIC) are typical metrics for stimulus electrodes but our chip architecture will place electrode materials anterior to photodiodes, thus a material with high transparency and biocompatibility must be determined.

These electrode characteristics have already been studied extensively in photovoltaics. Therefore in order to provide the best performance for our proposed device it is necessary to extensively test a selection of materials from previous literature. Each of the three categories: Trans-conductive Oxides (TCO), Metal Nanowires (NW), & 2-D materials can yield suitable candidates, such as: Aluminum doped Zinc Oxide (AZO), Boron doped Zinc Oxide (BZO), Indium Tin Oxide (ITO), AgNW/Silver Nanowires + PEDOT:PSS, Carbon Nanotubes (CNT) + PEDOT:PSS, & Graphene with PEDOT:PSS. The primary materials examined in this study are Aluminum doped Zinc Oxide (AZO), Boron doped Zinc Oxide (BZO), PEDOT:PSS for environmental sensors, PEDOT:PSS, and AgNW.

The fabrication of test electrodes has two separate wafer designs. The testing substrate used for electrocharacteristics has a Ti/Au/Ti sandwich structure on Si wafers; on a SiO2 layer 30nm Ti was sputtered, followed by 500nm Au, and then 30nm or Ti. A photoresist pattern was used with wet etching to create a desired wiring pattern. Next, a 1um SiO2 passivation layer was applied and reserved contact/ electrode locations were etched with RIE. Last, an experimental electrode material was sputtered onto the reserved electrode location. For the biocompatibility test and the transparency test, electrode material was sputtered onto 1mm thick quartz glass substrates. The resulting substrate was cut to specifications via optimized saw dicing. Optical testing utilizes the same substrate without dicing measures. Since our device will be mounted in ocular tissue for the long-term biocompatibility concerns become a central issue. An MTS biocompatibility assay test, using Hippocampal neurocytes, was performed on 10mm x 10mm square test substrates on quartz glass. AZO, BZO, & PEDOT:PSS electrodes were successfully formed and Pt and Ti electrode wafers were fabricated for baseline. In the biocompatibility test. Each conductive material is deposited on quartz pillars. The pillars have dimensions of 50um x 50um x 200um. Each pillar is spaced 200um X & Y from other pillars in a grid like fashion. This research currently is verifying the bi-compatibility of flagged materials and we will continue to report on electrode performance compared to referenced research. AZO was a promising material but with initial testing was shown to be incompatible. Statistically speaking AZO is less biocompatible than control condition so is incompatible with our application at this point in time. BZO and AgNW are also being targeted for Biocompatibility testing due to the potential of harmful nanoparticles from the electrode material. PEDOT-PSS is commended for its biocompatibility, electrical, & optical characteristics but process fabrication methods used can lead to undesirable material conditions like optical hazing in the polymer.

The Hippocampal neurocytes in direct contact with our electrode material showed biocompatibility of AZO to be lower than Pt electrodes. Further testing with BZO and AgNW are required because current literature suggests that each of the metallic materials has the potential to release hazardous nanoparticles to the tissue. Optical and electric characteristics have thus far been within expected performance ranges for our desired device.

2:30 PM SM01.03.06 Biomedical Applications of Wireless Surface Heater with Near-Field Communication Temperature Sensor Albert H.Y. Lau and Paddy K. L. Chan; The University of Hong Kong, Hong Kong, Hong Kong.

Hyperthermia (also known as thermal therapy or thermal ablation) has been adopted as one of the cancer treatment approaches in medical surgery. By applying high temperature on the cells, the proteins structure would be damaged and the cell would be destroyed. In general, Radio Frequency (RF) probes are applied onto the target tissues for the ablation process. However, one of the major drawbacks is difficult to apply when the cancer tissues are on the surface of the organs. Here we propose a novel approach to develop surface hyperthermia technique by using oscillating magnetic field induction on metal thin film. In our device, the heat is transferred from the organ surface to the cancer cells through bioheat transfer process. Heat generation process will be modulated by varying the conductance of the metal thin film, the strength and the frequency of the oscillating magnetic field. Optimal parameters such as film geometry, film thickness, magnetic induction distance and ablation time are identified through the combination of in vivo experiment and computational modelling. Near-field communication (NFC) temperature sensor is also integrated in the system enabling a wireless interface for smartphone to monitor and analyze the treatment performance. Based on the steady state heat transfer model and comparing the measured temperatures by the NFC temperature sensor, we can calculate the temperature profile inside the pig liver. By using a input power of 2000W/m2, the highest heater temperature is 443 K in our device which is sufficient for the ablation process. This wireless heater is believed to have high potentials in various kinds of in-vivo testing or non-invasive thermal treatments.

2:45 PM SM01.03.05 Nanowire Sensor Devices for Lab-on-a-Chip Platform Larysa Baraban1, 2, Julian Schlüt1, Bercy Ibarlucea1, 2 and Gianarelio Cuniberti1 2, 3; 1Institute for Materials Science, Max Bergmann Center for Biomaterials Dresden, TU Dresden, Dresden, Germany; 3TU Dresden, Center for Advancing Electronics Dresden, Dresden, Germany.

Tight interaction between nanophysics, materials science and biotechnology led to the emergence of a new class of bioinspired systems that enables to bring the area of biosensors e.g. for cell or molecular diagnostics and analytics to the new level. Very promising candidates for the future diagnostics are the electronic nanobiosensors that have attracted great attention in the last years since they provide rich quantitative information for medical and biological assays without pre-treatment and specific optical labelling of the detected analyte. One dimensional nanostructures, e.g. semiconductor and metallic nanowires serving as backbone of the sensor device, have attracted attention as highly efficient elements due to their high surface-to-volume ratio, which simplifies the detection of biochemical species. Use of nanowires enable to ultimately decrease the dimensions of the sensing area of the device and thus increase the resulting sensitivity of the assay. Finally, nanoscale sensors integrated into lab-on-a-chip system offer attractive opportunity of the multifunctional and multiplexed bio- and chemical analysis that can be performed in real time, directly in-flow. Here we focus on two subsystems for the in-flow analysis at the micro- and nanoscale, represented by (a) silicon nanowires based field effect transistor and (b) metal nanowires assembled as nanocapacitor. We demonstrate the applicability of the systems for the detection single molecules, e.g. influenza or Ebola viruses [1-3], biochemical reactions [4], as well as classify the blood cells in a cytometry format.

Circulating Tumor Cell Microarrays: An Emerging Tool in Cancer Diagnostics

By Xuan Zhang, Jin Hu, Qiu Xie, Bo Zhang, and Masoud S. Loeian

Wednesday Morning, April 24, 2019

In this presentation, we will discuss the use of microarray-based technologies for the detection of circulating tumor cells (CTCs) in blood samples. We will present our recent work on the development of a novel microarray system that is capable of capturing CTCs with high sensitivity and specificity. Our microarray system utilizes an innovative design that allows for the simultaneous capture of multiple CTC clusters, thereby improving the overall capture efficiency.

We have demonstrated the successful capture of spiked CTCs in blood samples, as well as the capture of CTC clusters in patient samples. These results highlight the potential of our microarray system for application in clinical settings, particularly in the early detection and monitoring of cancer.

The presentation will also include an overview of the current state of CTC research and the challenges that remain in this field. We will discuss the potential impact of our work on the development of new diagnostic tools and therapeutic strategies for cancer patients.
Carbon dots, a new class of zero-dimensional carbon-based nanomaterials, have attracted great interest recently in the nanomedicine because of their versatile merits such as biocompatibility, facile functionalization, and tunable photoluminescence properties. In particular, carbon dots have allowed for their biomedical applications to disease diagnostics and therapeutics such as bioimaging and photodynamic therapy. Here, we present the new design of carbon dots with multiple functions that highly inhibit the aggregation of metalloproteins and form Au(A) peptides. The abnormal assembly and aggregation of Aβ peptides in the brain tissue is a major hallmark of Alzheimer’s diseases (AD) that currently affects one in nine people aged over 65 worldwide. Despite numerous efforts made over the past decades, effective suppression of Aβ aggregation is still challenging due to multifactorial pathogenesis involving high levels of metal ions in the brain. Note that copper ions (Cu(II)) have drawn significant attention in AD pathogenesis due to their high activities in binding with Aβ peptides and forming neurotoxic Aβ-Au(Cu) complexes.

To provide a new anti-amyloidogenic strategy in the prevention of Cu(I)-associated Aβ aggregation, we have synthesized the multifunctional carbon dots and demonstrated their capabilities on (i) effective Cu(I) coordination; (ii) interaction of Aβ self-assembly; and (iii) photodynamic inactivation of Aβ peptides. The nitrogen-containing aromatic moieties on as-prepared carbon dot’s surface can act as a key role in interact with Cu(II) and Aβ’s aggregation sites by electrostatic and hydrogen/hydrophobic interactions. Interestingly, the Cu(II) coordination of carbon dots promotes the carbon dots’ absorption and fluorescence enhancement, thus further leads the photoinduced generation of reactive oxygen species (ROS) under light irradiation; the resulting ROS from carbon dots then photodynamically inactivated Aβ peptides (e.g., histidine and methionine) to lose the affinity towards Cu(II) as well as an aggregative property. These carbon dots’ simultaneous and multiple inhibitory effects significantly mitigated the neuronal cytotoxicity of Cu(II)-bound Aβ species, showing high cell survival rate.

In summary, we will introduce the synthesis of multifunctional carbon dots and the various photochemical analyses to validate the suppressing capabilities of carbon dots against Aβ aggregation. Our investigations highlight the significant luminescence properties of carbon dots as promising biocompatible nanoeagents and their therapeutic application in preventing Aβ-induced Alzheimer’s diseases.

8:30 AM  3SM01.04.02
Cancer Nanotheranostics Based on Molecular Self-Assembly Process   Xiaoyuan Chen; National Institute of Biomedical Imaging and Bioengineering, Bethesda, Maryland, United States.

The Nobel Prize in Chemistry 1987 was awarded to Cram, Lelh and Pedersen for their development and use of molecules with structure-specific interactions of high selectivity. Twenty years later in 2016, Nobel Prize in Chemistry recognized supramolecular chemistry and molecular recognition again by awarding Sauvage, Stoddart and Feringa for the design and synthesis of molecular machines. This talk takes cyclodextrin and cucurbituril as examples to develop cancer nanotheranostics that make use of the dynamic and responsive nature of non-covalent interactions. By the formation of host–guest complexes with macrocyclic hosts, the anticancer drugs can be easily formulated to prepare nanomedicine showing satisfactory anti-tumor efficacy and reduced normal organ toxicity.

9:00 AM  3SM01.04.03
Re-Purposing of Frog-Skin Derived Collagen for Wound Healing Applications   Cidiem Cimenoglu; Jun Kit Wang and Chor Yong Tay; 1, 2 School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore; 3School of Biological Sciences, Nanyang Technological University, Singapore, Singapore.

Collagen (Col) is a well-studied biomaterial, particularly as wound dressing material due to its superior biological and chemical properties [1]. However, the application of collagen in wound healing remains as a critical issue due to poor adhesion, proliferation and migration of cells. In addition, majority of the collagen-based biomaterials are primarily fabricated from mammalian sources, such as bovine and porcine [2]. There have been many considerations in terms of religious issues. Moreover, the extraction process from mammalian animals is complex, laborious, time consuming and expensive due to the stiff and fibrous nature of bovine and porcine tissue [3]. Hence, alternative sources of collagen are highly desirable, particularly for wounds treatment.

In this study, collagen derived from the skin of the American Bullfrog (i.e. Rana catesbeiana) is explored as nature-derived biomaterials for wound healing applications. We report the successful implementation of an innovative method that can significantly shorten the collagen extraction process by ~50% compared to traditional acid solubilisation method with relatively high extraction yield (~35%). Differential scanning calorimetry (DSC) analysis suggest that the collagen has excellent thermal stability (~41°C), suggesting that it is compatible for skin-contacting as well as for in vivo implantation applications. In vitro studies showed that the bioactivity of the bullfrog skin-derived collagen was well-preserved by supporting the attachment and proliferation of human keratinocytes (i.e. HaCaT), compared to commercially-available bovine collagen. Interestingly, our findings demonstrated that the extracted bullfrog skin-derived collagen can significantly enhanced the wound closure rate of HaCaT in an in vitro scratch wound assay as compared to bovine collagen. At the mechanistic level, we showed that this phenomenon may be attributed to the ultra-fine nano-fibers of the frog-skin derived collagen, which could augment the process of re-epithelialization by modulating the adhesiveness and chemotaxis of the keratinocytes [4]. Overall, bullfrog skin could be a viable waste-to-resource material for the production of non-mammalian collagen with high yield percentage and great wound healing capacity.

References

9:15 AM  3SM01.04.04
A Biodegradable Hybrid Nanoplatform for Synergistically Overcoming Multidrug Resistance   Shengjiao Wang; 1, Ki-Bum Lee and Qiuyi Zhang; 2 Rutgers, The State University of New Jersey, Piscataway, New Jersey, United States; 3Northwestern Polytechnical University, Xi’an, China.

The complexity and heterogeneity of cancer and subsequently developed multidrug resistance (MDR) seriously undermines the therapeutic potential of chemotherapy. Herein, we developed a biodegradable redox heat assisted cancer killing (RHACK) nanoparticle for enhanced treatment of cancer in vitro and in vivo. Unlike conventional anticancer strategies, our hybrid nanoparticle based drug delivery system (DDS) not only target-specifically delivers anti-cancer reagents, but also target heterogenous MDR pathways to achieve sensitization of cancer cells. More specifically, our RHACK nanoparticle-based drug delivery system (DDS) reduces intracellular glutathione (GSH) level, induces ROS generation and simultaneous provide photothermal (PTT), thereby synergistically sensitizing breast cancer towards chemotherapy. Remarkably, our RHACK nanoparticle is constructed from an iRGD conjugated hollow iron oxide core and a manganese dioxide shell (Fe3O4/C@MnO2@iRGD NPs) and shows unique benefits for synergistically overcoming MDR: i) a strong NIR absorption for effective laser ablation of tumor and sensitize the tumor to further chemotherapy; ii) a tunable glutathione-reactive MnO2 shell; iii) a redox-based endogenous biodegradability; iv) a hollow structure for efficient anti-cancer drug loading; v) Fenton reaction and ROS species (hydroxyl radical); vi) Mn4+ as degradation product for induction of intracellular Fenton reaction and ROS species (hydroxyl radical); vii) capabilities of breast tumor targeting and penetration. Based on this unique platform, we successfully demonstrated a robust co-sensitization of a malignant drug resistant breast cancer towards a clinical applied anti-cancer drug in vitro and in vivo by combining PTT, glutathione reduction and Fenton reaction on a single platform. A detailed mechanistic study on the molecular biology pathways further reveals the synergy originate from the regulation over several key genes and proteins including HSF-1 and MDR-1/P-gp, TP53, BCL-2, BAX, Caspase 3/9. Given the heterogeneous tumor microenvironments and the highly complicated drug-resistance pathways in breast cancer, our multifunctional hybrid nanoparticle-based DDS could provide a promising therapeutic alternative for more efficient treatment of breast cancer in clinical applications.

9:30 AM  3SM01.04.05
Top-Down Fabrication of Spatially Controlled Mineral Gradient Scaffolds for Interfacial Tissue Engineering   Alexander Boys; 1, Hao Zhou, 1 Jordan Harrod, 2 Lawrence Bonassar, 1 and Lara Estoff; 4; 1Materials Science and Engineering, Cornell University, Ithaca, New York, United States; 2Ming exposed School of Biomedical Engineering, Cornell University, Ithaca, New York, United States; 3Sibley School of Mechanical Engineering, Cornell University, Ithaca, New York, United States; 4Kavli Institute for Nanoscale Science at Cornell, Comin, University, Ithaca, New York, United States.

Materials engineering is typically divided into “bottom-up” and “top-down” methodologies. While, top-down engineering has been common practice for centuries, these approaches are rarely used with respect to biological systems. We have applied a top-down approach for generating a mineral gradient scaffold in trabecular bone. Mineral gradients are found in a variety of biological systems that link soft tissue and bone. Some of these systems are primarily mechanical, such as the attachments of ligaments and tendons with bone or the interface between cartilage and bone. Other soft tissue-to-bone interfaces are necessary for development, such as the growth plate or the interface present
during endochondral ossification. These interfaces are further relevant to cancer metastasis, as tumors have been found to localize to the growth plate. These systems are complex, requiring a method for producing the mineral gradient present at the interface. With these goals in mind, we fabricated a mineral gradient scaffold through the spatially controlled removal of mineral from bone.

To fabricate this scaffold, cylindrical trabecular bone biopsies were extracted from neonatal bovine femurs. These biopsies were decellularized, followed by partial submersion in a demineralizing solution. Scaffolds were removed from the demineralizing solution at time points of 0, 3, 6, and 9 hours to determine the amount of mineral removed from the biopsy and observed to be the porosity in the trabecular bone. These observations were confirmed by plotting porosity vs. time or the fractional demineralized content and fitting a surface to these data. Scaffolds were segmented into quadrants, and X-ray diffraction was performed on these segments, confirming the presence of a mineral gradient within the scaffold.

To examine the cellular compatibility of the resulting mineral gradient, mesenchymal stem cells were seeded onto these scaffolds. The seeded mineral gradient scaffolds were cultured in osteogenic media, and a live/dead stain was performed. The cells attached to the exterior of the trabecular structure with a viability of ~91%. The scaffolds exhibited high viability and with no differences in viability were observed in the mineralized or demineralized portions of the scaffolds.

Immunohistology was performed to examine the effects of mineral content on cellular behavior. Seeded scaffolds were cultured, fixed, and sectioned for staining. Stains were chosen to determine if stem cells were showing any chondrogenic or osteogenic behavior. Staining profiles revealed differences in cellular behavior between the mineralized and demineralized ends as well as on the exterior and interior of the scaffold. Type I collagen staining was observed throughout the scaffold. Type II collagen staining was consistent on the interior of the scaffold but appeared higher in the exterior regions of the mineralized end of the scaffold versus the demineralized end. Alkaline phosphatase staining was consistent on the exterior of the scaffold but appeared higher on the mineralized interior versus the demineralized interior. These findings reveal that the presence of a mineral gradient drives stem cells to produce proteins associated with chondrogenic and osteogenic cellular behavior.

Overall, we fabricated mineral gradient scaffolds using a top-down engineering approach. These scaffolds, generated using a novel approach to biomaterials synthesis, drive cellular behavior and will be useful in a variety of fields, including orthopedics, development, and cancer research.

Quantum Capacitance Based Amplified Graphene Phononics for Studying Neurodegenerative Diseases

Bijitimala Keisham1, Akop Seksenyan2; 1, Steven Denyer2, Pouyan Kheirkhahi3, Gregory D. Arnone2, Pablo Avalos3, Abhiraj D. Bhimani2, Clive Svendsen4, Vikas Berry1 and Ankit Mehta7; 1Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois, United States; 2Neurosurgery, University of Illinois at Chicago, Chicago, Illinois, United States; 3Chicago Medical School, Rosalind Franklin University of Medicine and Science, North Chicago, Illinois, United States; 4Regenerative Medicine Institute, Cedars-Sinai Medical Center, Los Angeles, California, United States.

Amyotrophic lateral sclerosis (ALS) is the most common adult-onset motor neuron disease, characterized by a rapid loss of upper and lower motor-neurons resulting in patient death from respiratory failure within 3-5 years of initial symptoms onset. Although at least 30 genes of major effect have been reported, the pathobiology of ALS is not well understood. There is a critical need to develop a system which can accurately diagnose this rapidly deteriorating disease. Herein, we report on graphene’s phonon vibration-energies as a sensitive measure of the composite dipole moment of the components of the interfaced cerebrospinal fluid (CSF) to specifically identify patients with ALS disease.

The second-order overtone of in-plane phonon vibration energy (2D) of graphene shifts by 3.2±0.5 cm⁻¹ for all ALS patients studied in this work. Further, the amount of -doping induced shift in phonon energy of graphene, interfaced with CSF, is specific to the investigated neurodegenerative disease (ALS, Multiple Sclerosis and Motor Neuron Disease). By removing a severe roadblock in disease detection, this technology can be applied to study diagnostic biomarkers for researchers developing therapeutics and clinicians initiating treatments for neurodegenerative diseases.

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Overall, we fabricated mineral gradient scaffolds using a top-down engineering approach. These scaffolds, generated using a novel approach to biomaterials synthesis, drive cellular behavior and will be useful in a variety of fields, including orthopedics, development, and cancer research.

Nanolithographically Patterned Surfaces for Quantifying Cellular Adhesion, Migration and Communication

Marc Raphael, Joseph A. Christodoulides, Michael Robitaille, Jinny Liu, Marc Christophersen and Jeff Byers; U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Cells are continuously performing chemical computations based on a range of inputs from their immediate environment. Two fundamental phenotypes that result from these computations are cell adhesion and migration, which play central roles in development, wound healing and diseases such as cancer. The degree to which cells adhere or migrate is dependent upon a combination of chemical and physical properties of the substrate. However, the complex coupling amongst these physical and chemical cues has made it challenging experimentally to deconvolve their individual contributions. Furthermore, cells dynamically alter their environment by the secretion of proteins. To address these complexities, we have employed a combination of electron beam and optical lithographic techniques to fabricate substrates which incorporate independently tunable topographical and chemical signaling cues, as well as nanosensors for detecting cell secretions. The approach works by patterning two materials on a single chip, one for topography, and the other for chemical functionalization. The first material, quartz, is light microscopy compatible and can be dry etched for 3D topography formation. The second material, gold, is patterned independently of the quartz etching process into nanostructures for use in either interfacing with the cell membrane or detecting protein secretions. I will present results on a range of cell types cultured on multiplexed substrates that integrate nanosensors for quantifying single cell secretions, topographical patterns for directing cell migration and biofunctionalized nanostructures for targeted adhesion studies. Cells at the boundary of two patterns experience a surface-induced competition that can be tracked in real time as they decide to adhere to one surface or migrate to the other. These chips enable quantitative insight into the biology of how local environments influence cellular decisions as well as potential guidance in the design of next generation wound healing materials and implants.

In Vitro Study for Pressure- and Cavitation-Induced Cell Damage During Mechanical Impact

Woromo Kang, Michael Robitaille and Marc Raphael; Naval Research Laboratory, Washington, District of Columbia, United States.

The dynamic response of cells when subjected to mechanical impact has become increasingly relevant for accurate assessment of potential blunt injuries and understanding injury mechanisms. When exposed to a blast, ballistic, or impact, a biological system, e.g., human brain or skin, is rapidly accelerated, which results in an acceleration-induced pressure gradient. In order to study cell behavior under these threats, we have developed a new experimental method that applies a well-controlled mechanical impact to live cells cultivated in a custom-built in vitro setup compatible with live cell microscopy. A drop tower system is utilized to apply the mechanical impact while concurrently visualizing each impact using high speed cameras. The impact amplitude is controlled by changing the vertical height of a movable mass, i.e., drop height, which is then accelerated toward the setup once released. Our experiments show that the maximum pressure in the in vitro setup is very sensitive to the height of cell culture media. As an example, we experimentally correlated drop heights with the onset of cavitation nucleation in different cell culture setups. We find that the critical drop height decreases by about 7 times when the height of cell culture media increases from 1 cm to 4 cm. This result indicates that lower drop heights induce the critical pressure (a material related property) with increasing cell media height and, as a result, implies that impact-induced pressure in biological systems depends on their size due to inertial effects. Another interesting experimental observation is that cells near cavitation bubbles upbaked tripodium iodide, typically not permeable to live cells, which we suspect is due to transient damage to the cell membrane. Our study shows that in addition to acceleration - which is the most commonly used criteria for blunt injury - size of biological systems, e.g., head size, should be appropriately considered for accurate assessment of potential injuries due to mechanical impact.

Gum—Tragacanth-Alginate Beads as an Oral Nutraceutical Delivery System for Improving the Bioavailability of Nutraceuticals

Anupam Apoorva1, Abhiraj D. Bhimani2, 3, Manchikanti Padmavati2 and Swagata Dasgupta2; 1School of Bioscience, Indian Institute of Technology Kharagpur, Kharagpur, India; 2Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, India; 3Rajiv Gandhi School of Intellectual Property Law, Indian Institute of Technology Kharagpur, Kharagpur, India.

The present study delineates preparation, characterization, and application of calcium alginate (CA) - Gum tragacanth (GT) beads carrying phenolic compounds from B. alba plant for oral drug delivery. The CA-GT beads were prepared by ionic gelation method and its physicochemical characterization was carried out by SEM, EDAX and FTIR analysis. The swelling analysis and in vitro degradation assay revealed that the percentage of swelling at different time points varies with the respective change in the GT concentrations in beads. Variation was prominent in compositions with higher GT concentrations.

A critical examination of the drug release profile showed correlation with the percentage of GT in the formulation that retarded the release rate of phenolic compounds. Extract loaded formulations were tested against osteosarcoma cells (MG-63). Cytotoxicity data, live dead staining, nuclear condensation-frAGMENTATION, DNA fragmentation (by TUNEL assay) and cell
migration study together confirmed the therapeutic potential of the CA-GT formulations. The above findings suggest that *B. alba* phenolic extract loaded CA-GT beads could be used as the natural therapeutic source for cancer treatment and an ideal source of nutraceuticals.

11:30 AM SM01.04.10
**Diagnosis of Vitiligo Through Novel UV Camera Applying Eco-Friendly Blue-Light Emitting Zinc-Blended Quantum-Dot**
Jiho Choi, Il-Hwan Kim, Jun-Sung Park and Jeou-Gun Park; Department of Electronics and Computer Engineering, Hanyang University, Seoul, Korea (the Republic of).

In general, the vitiligo is diagnosed by wood lamp test which is also known as ultraviolet (UV) light test. However, UV light in the wavelength under 400-nm is not visible to the human eyes and cameras. Thus, it is difficult to obtain accurate UV images for analyzing lesions of vitiligo patients. The light incident into the human skin has different penetration depth depending on the wavelength, which means the information of the reflected light differs according to the incident light wavelength. If there were any cameras or sensors that are capable of obtaining UV reflected images of the lesion, more deliberate information such as lesion size, depth, and shape could be obtained through a depth profile according to the penetration depth of human skin along the wavelength.

Here, we developed a novel UV camera applying blue-light emitting quantum-dots (QD) to conventional Si CMOS image sensor (CIS). Synthesized zinc-blend-structure QD absorbs UV light below 400-nm wavelength and emits the 433-nm-wavelength blue-visible-light by energy-down-shift mechanism, having a quantum yield of 75.2%, full-width half maximum (FWHM) of 20.7 nm. The reflected light from the object passes through the QD filter before entering the photodiode of the Si CMOS image sensor. The QD filter completely passes the visible light and only absorbs UV light and QD emits the blue-visible-light. In other words, the QD filter converts UV light, which the conventional image sensors cannot detect, into the blue light so that the image sensor can detect it. This process presents that the image sensor receives a further increased blue pixel’s signal caused by UV intensity. The difference of blue pixels intensity between with and without QD filters can be considered as a detected UV intensity.

In this work, we diagnosed and treated lesions of 2 vitiligo patients through our new QD UV camera. We photographed the UV images of their hands and faces and analyzed them in cooperation with dermatologists. Based on the analysis, we recommended proper treatment and they tracked their treatment progress for 2 months. It was observed that the UV images of the vitiligo lesions showed lower UV pixel intensities than the intact normal skin, which means that the location, size and distribution of vitiligo lesions could be clearly identified through the UV image. The UV pixel intensities effectively showed information of epidermis and dermis where vitiligo lesions mainly exist. Melanocytes reflect and scatter ultraviolet rays to protect the skin from harmful UV rays. So, in UV images of normal skin, melanocytes reflect UV, resulting in high UV intensity. However, in the case of vitiligo lesions, there is less reflection of UV light due to the lack of melanocytes, resulting in low UV intensity. In addition, we can also estimate the extent of melanin pigment deficiency by this UV intensity analysis. The regions with relatively high UV pixel intensity and those with relatively low UV intensity were clearly distinguished in the vitiligo region. The relatively lower UV intensity is relatively large, indicating that lesions are more severe. We confirmed that the novel QD UV camera can accurately discriminate the lesions of vitiligo from the intact region, and also can quantify the severity of the lesion. It is expected that the UV images taken by the QD UV camera will provide guidelines for the diagnosis and treatment of vitiligo. In addition, UV pixel analysis is also considered to be valid for several skin disorders that can be diagnosed by the UV light test such as tinea capitis, erythrasma, albinism, etc.

*This work was financially supported by the Brain Korea 21 Plus Program in 2018.*

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1:30 PM SM01.05.01
**Point-of-Care Device for Detection and Measurement of Biomarker Associated of Trauma Brain Injury**
Stephany Uribe, Alexander Rodriguez, Eliana Cervera and Pedro J. Villalba; Universidad del Norte, Barranquilla, Colombia.

Trauma brain injury (TBI) is a problem in public health locally and globally. The consequences of this pathology are serious and its mortality rate is high. TBI severity is classified using the Glasgow coma scale. This scale assigns points to the patient’s eye opening, motor and verbal response based on a qualitative test. Although this method is part of several TBI protocols, its application is susceptible to errors associated to the specific physiological response of each person. Misclassification of the initial TBI severity will in turn impact the therapeutic management causing in many cases delays in proper treatment. In this research work, we are proposing a quantitative method to classify the severity of the TBI, using highly specific serum biomarkers in order to reduce misclassification as well as to provide a fast, easy to use tool for monitoring the patient’s progress. An electrochemical immunosensor has been developed by means of a specific antibody against S100B protein. S100B is a calcium binding protein present in the central nervous system; its concentration increases within the initial hours of the TBI event, its value as TBI biomarker has been demonstrated before. The biosensing platform was created by electrochemical polymerization of a nanodiamond enhanced polyaniline matrix, this matrix was then functionalized with antiS100B by crosslinking reaction after APTMS-GA (siloxane 3-aminopropyltriethoxysilane - glutaraldehyde) initial surface modification. The amount of antibody was optimized for the specific surface active area using different depositing dilutions, the results showed that after 5ug/mL no statistically significant increment in the electrochemical signal is observed. Response of the biosensor to the antigen was recorded using impedence spectroscopy experiments in 0.2 M KCl and 10 mM potassium ferrocyanide as supporting electrolyte. Our results showed the characteristic semicircle behavior at the high frequency range associated to the redox probe of the electrolyte; also, the Warburg line has been observed at the low frequency range.

1:45 PM SM01.05.02
**Hydrogel-Based 3D Cell Culture Models of Neurological Diseases—Disease Progression and Experimental Therapeutics**
Sara Pedran, Jee-Wei Chen, Jan C. Lumibao, Ana M. Magarinos, Donald W. Pfiff, Jann N. Sarkaria and Brendan A. Harley; 1University of Illinois at Urbana Champaign, Urbana, Illinois, United States; 2Mayo Clinic, Rochester, Minnesota, United States; 3The Rockefeller University, New York, New York, United States.

Functional brain changes represent a significant social and economic burden that has increased considerably over the last decades. The development of new scientific capabilities that are able to analyze brain structure and connectivity has recently revitalized the neuroscience field. Biomaterial based ex vivo models of healthy and diseased brain tissue are among those tools that may help study the complex in vivo brain tissue to better diagnose, treat and develop experimental drugs. Recently, we have developed a novel biomaterials based on methacrylamide-functionalized gelatin hydrogels, and used microfluidic-forming techniques to generate platforms that combine transitions of biophysical and biomolecular properties found in the glioblastoma tumor microenvironment, from the core to the tumor margins (2). Moreover, this biomaterial approach is able to monitor the response of patient-derived xenograft (PDX) cell populations with different molecular signatures; in particular, we have analyzed the amplified and the constitutively activated vIII mutant EGFR receptor. We have also characterized PDX response to targeted inhibitors, such as erlotinib, a tyrosine kinase inhibitor that specifically blocks EGFR.

In addition to tumor tissue samples, these gelatin-based platforms permitted the survival and growth of the large nucleus gigantocellularis (NGC) neurons, considered as the ‘master cells’ for initiating CNS arousal. The better understanding of NGC neurons might help to understand particular characteristics of certain brain disorders (7). Until now, the lack of a physiologically relevant microenvironment for in vitro culture has been associated with unusual cell morphologies and cell death. We showed that NGC neurons were able to survive and differentiate in the presence of HA, and without the assistance of growth factors (8). In this context, 3D in vitro cultures of NGC neurons may allow the analysis of the extracellular matrix contributions and growth factors to their survival, growth and development. Due to the success of these platforms to recreate cerebral tissue peculiarities, we have also cultured neural stem cells within gelatin—HA hydrogels and we are currently working on the development of neurodegenerative diseases models.
References

2:00 PM SM01.05.03
Self-Powered Biosensors—Integration of p-n Junction Photodetectors with Colorimetric Reactions Kihyeun Kim, Hyungjin Jang and Min-Gon Kim; Department of Chemistry, Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Electronic devices are one of the most promising candidates for chemical and biological sensor platforms because of their high sensitivity, and application to Internet of Things (IoT). However, a major challenge to developing such sensor systems is the use of battery power owing to its limited life-time, inconvenience of recharging, and insufficient battery level to operate the integrated sensor system.

In this study, we suggest self-powered biosensors by integration of n-IGZO/p-Si photodetectors and enzyme-based colorimetric reactions, which are operated by light sources in daily life environment such as fluorescent light and sunlight. A colorimetric reaction was performed at a polydimethylsiloxane vessel located at the upper side of the IGZO/Si photodetector, which is physically apart from the photodetectors. Photocurrent changes of the photodetectors are induced by the colorimetric reaction depending on target concentration, which enables quantitative analysis. The self-powered biosensors showed high sensitivity towards glucose level in real human samples without matrix effect due to physical separation of the photodetectors and colorimetric reaction part. This sensor platform could pave the way for highly sensitive portable IoT biosensors operating without batteries.

2:15 PM SM01.05.04
Anti-Adhesive Bio-Degradable Mg Alloy Assisted by Nano-SiO₂ Particles Jaehyoung Son¹, Junkyun Oh¹, Daehyun Cho² and Winfried Teizer³; °Texas A&M University, College Station, Texas, United States; ²R&D Center, Hyundai-Steel, Dangjin, Korea (the Republic of).

Recently the interest in bio-degradable Magnesium alloys as an alternative implant material has increased. Since no surgery is needed to remove the inserted implant, the risk of bacterial infection and the medical burden is decreased. In particular, anti-adhesion is one of the prerequisite properties in medical applications to avoid bacterial colonization on the implant. In this study, biocompatible Mg-Zn-Ca alloys are synthesized by squeeze casting and hydrophobic nano-SiO₂ particles are coated on the alloy surface. In the process, a porous SiO₂ layer is formed and its condition controlled via dip-coating. The human pathogen most frequently found on implant materials, Staphylococcus Aureus (S. Aureus), is prepared through the porous-plating method to evaluate the anti-adhesive properties and the bacteria on the surface are counted by scanning electron microscopy. The result shows that hydrophobically treated SiO₂ particle layers significantly mitigate the bacterial attachment compared to a bare Mg surface and a SiO₂ particle layer.

2:30 PM BREAK

3:30 PM SM01.05.05
Development of Tissue-Engineered, Disease-Mimicking Culture Platforms Kristyn Masters; University of Wisconsin, Madison, Wisconsin, United States.

Introduction: Extracellular matrix (ECM) alterations accompany the onset and progression of many diseases. In this work, we sought to develop tissue engineering-based approaches to mimic the disease environment in order to perform prospective analyses that probe the mechanistic role of the ECM in disease etiology. Our specific focus was on calcific aortic valve disease (CAVD), whose pathogenesis is poorly understood, but is known to involve excessive glycosaminoglycan (GAG) accumulation early in the disease process. We implemented two different strategies to create tissue-engineered platforms that mimic elements of early CAVD: 1) construction of engineered environments using traditional “bottom-up” methods, which enable tuning and control of scaffold parameters but fail to capture the complexity of the native tissue. 2) construction of a top-down organ culture platform that retains native complexity, but lacks the ability to precisely control tissue composition.

Methods: To create scaffolds via the bottom-up approach, we copolymerized methacrylated gelatin with either methacrylated hyaluronic acid (HA) or chondroitin sulfate (CS) at concentrations intended to replicate the GAG enrichment found in early CAVD (1x GAG = healthy valve; 4x = diseased) and seeded them with valvular interstitial cells (VICs). To create top-down scaffolds, we transduced scaffolds to overexpress hyaluronic acid synthase-3, an enzyme responsible for HA synthesis. Porcine aortic valve leaflets were treated with feline immunodeficiency virus (FIV) containing a vector for either GFP (FIV.GFP) or human hyaluronic acid synthase-3 (FIV.HAS3) and then cultured for up to 7 days. Cultures were also treated with low density lipoprotein (LDL) or oxidized LDL (oxLDL), which mimicked CAVD risk factors, and analyzed for overall ECM composition, compressive modulus, cell phenotype, and cytokine/growth factor production.

Results: Analysis of CS-enriched scaffolds demonstrated that pathological CAVD enrichment alone was sufficient to promote a change in VIC phenotype or secretion of inflammatory factors. Instead, the main function of increased CS appeared to be sequestration of oxLDL. Sequestered oxLDL increased the secretion of multiple inflammatory cytokines (e.g., IL-6, IL-8, PDGF-BB, MCP-1) by VICs, thereby implicating oxLDL as a potent factor in regulating pathological VIC behavior. Moreover, a positive feedback loop was uncovered where oxLDL increased CS production, which further increased oxLDL retention. These findings suggest that increased CS in early CAVD plays a central role in regulating the onset of inflammation.

Meanwhile, a different role for HA enrichment was demonstrated in both bottom-up and top-down scaffolds. ECM-edited valve organ cultures were generated to achieve a 4-fold enrichment in HA content, with the level of HA enrichment regulated by the amount of virus administered. This result demonstrated the ability to tailor the ECM composition of intact, 3D tissues, thereby providing a novel disease-mimicking culture platform. In both culture approaches, HA enrichment served to stimulate vascular endothelial growth factor (VEGF) production by the VICs, but HA was not involved in LDL/oxLDL sequestration or subsequent inflammatory activity. Instead, HA-induced VEGF production was sufficient to stimulate the proliferation and tubulogenesis of endothelial progenitor cells, suggesting that increased HA in early CAVD may promote the pathological angiogenesis that is a hallmark of this disease.

Conclusions: We developed complementary tissue-engineered platforms to mimic disease pathogenesis, including a novel approach to use intact organ cultures as semi-tunable biomaterials. These platforms were applied to reveal new information about CAVD pathogenesis. The applications of these approaches extend beyond valvular disease, as there are many pathways which involve selective enrichment of specific ECM components.

4:00 PM SM01.05.06
Radioluminescent Nanoparticles for Molecular Imaging and Theranostics Yufu Ren, Justin Rosch, Allison DuRoss, Madeleine Landry, Megan Neufeld and Conroy Sun; Oregon State University, Portland, Oregon, United States.

Molecularly targeted nanoparticles that produce X-ray excited optical luminescence, also known as radioluminescence, enable unique multimodal imaging capabilities not available with current clinical technologies. These functional nanomaterials, often comprised of lanthanide-doped nanophosphors, have also been evaluated as energy mediators for deep tissue photodynamic therapy (PDT) and other X-ray stimulated therapies. As both imaging probes and therapeutic, the application of radioluminescent nanoparticles (RLNP) is limited by their photophysical properties. Here we present the synthesis and characterization of lanthanide-doped nanoparticles with core-shell structure, incorporation of high-Z elements, and their surface modification with biocompatible polymers to improve functional properties for biological applications. In this radioluminescent platform, optical emission can be tuned by selection of dopants, such as Eu³⁺ and Tb³⁺. Utilizing a thermal degradation of organometallic precursors, uniform cubic (~11 nm) nanocrystals were obtained and observed by transmission electron microscopy (TEM). To evaluate the radioluminescence of these nanophosphors a suspension of the particles was irradiated at 130 kV while an emission spectrum was obtained by a spectrophotometer. Emission was improved significantly through protection from surface quenching of luminescent centers. In
Bioengineered 3D Interpenetrating Collagen-Alginate Network to Elucidate the Effects of Biomechanics on Cancer-Associated Fibroblasts (CAFs) Behaviour

Huan Cao and Chor Yong Tay; School of Materials Science and Engineer, Nanyang Technological University, Singapore, Singapore.

Cancer-associated fibroblasts (CAFs) are one of the major types of stromal cells within the tumor microenvironment that support tumor progression by secreting pro-tumorigenic cytokines. In addition, CAFs also play a key role in stromal remodeling during tumor progression, including increased deposition and crosslinking of collagen. In general, the matrix mechanics have been shown to affect various cellular behaviors. However, to our knowledge, limited studies have been carried out to investigate the effects of matrix biomechanical changes on CAFs behavior, particularly in three-dimensional (3D) environment as well as the downstream paracrine crosstalk with the surrounding tumor cells remains elusive. Hence, in this study, a collagen/alginate interpenetrating network (CoAI-IPN) hydrogel system was employed to investigate the phenotypic and functional characteristics of CAFs under 3D environment setting. In general, collagen and alginate have different crosslinking mechanisms, which will allow the precise control of the hydrogel biomechanical properties without affecting its biochemical properties.

Results showed that hydrogel with Young's Modulus from ~108 to 898 Pa was successfully fabricated by varying the crosslinking density of alginate which preserving the biochemical properties. Subsequently, CAFs were encapsulated within the CoAI-IPN hydrogel system. Interestingly, a highly polarized CAFs morphology was observed within compliant CoAI-IPN hydrogel (i.e. uncrosslinked system), but not rigid hydrogel system (i.e. highly crosslinked). This in contrast to 2D cell culture findings, in which stiffer substrate will promote the cell spreading. In addition, the compliant CoAI-IPN hydrogel system also affected the CAFs behavior at molecular level with enhanced nuclear translocation of the mechano-sensitive YAP/TAZ protein and expression, as well as the up-regulation of other CAFs classical markers (i.e. α-SMA and FAP). These findings show that the CAFs phenotype and functional characteristics are highly plastic, which depends on the biomechanics of the microenvironment. Moreover, these understanding from the tumor stroma mechanic-bioactivity relationship studies can shed the lights on the restraint the pro-tumorigenic effects of CAFs in cancer therapy.


Additively Manufactured Scaffolds with Selective Permeability for Biological Applications

Yale Jeon, Min Soo Jeon and Dong Rip Kim; Hanyang University, Seoul, Korea (the Republic of).

Three-dimensional (3D) porous scaffolds with large specific surface area have received considerable interest due to their capabilities of effective cell attachment and growth. For their utilization, the cells are cultured over the pre-fabricated scaffolds, which typically not only accompanies a long-time process, but also arises the challenge to precisely position target cells inside the scaffolds. Here, we utilize an additive manufacturing technique to fabricate nanoporous 3D porous scaffolds in which target biological species are located. The fabricated platform shows the selective permeability such that biological species are confined inside, while chemical species can pass through the porous layers, due to the compliant CoAl-IPN hydrogel system also affected the CAFs behavior at molecular level with enhanced nuclear translocation of the mechano-sensitive YAP/TAZ protein and expression, as well as the up-regulation of other CAFs classical markers (i.e. α-SMA and FAP). These findings show that the CAFs phenotype and functional characteristics are highly plastic, which depends on the biomechanics of the microenvironment. Moreover, these understanding from the tumor stroma mechanic-bioactivity relationship studies can shed the lights on the restraint the pro-tumorigenic effects of CAFs in cancer therapy.

Acknowledgement

This work was supported by the Intelligent Synthetic Biology Center of Global Frontier Project of the National Research Foundation of Korea (NRF-2012M3A6A8054889), funded by the Ministry of Science and ICT of the Republic of Korea. This research was also supported by “Human Resources Program in Energy Technology” of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 20184010201710).

Magneto-Dielectric Hyperthermia Therapy for Adenocarcinoma

Sovesh Mohapatra, Naveen K. Tailor and Soumitra Satapathi; Indian Institute of Technology, Roorkee, India.

In the last few decades, adenocarcinoma has become a major cause of death for millions. Different forms of tumor therapies are in use including chemotherapy and radiotherapy but due to inefficacy of these therapies, it has elicited considerable research interest to explore alternative methods. The use of regional hyperthermia for the treatment of adenocarcinoma can negate the use of harmful chemicals and radiations. In the present study, Ca0.6Fe0.4O3-PVDF has been proposed as the bio-compatible magnetic dielectric composite to provide thermo-regulated prolonged treatment. In a systematic manner, the study has attempted to optimize the bio-compatible magnetic hyperthermia and dielectric thermo-regulation parameters by analyzing a group of composites. Finite Element Method (FEM) analysis has been used to simulate hyperthermia treatment of adenocarcinoma in the glandular cells of prostate gland. Electromagnetic Waves (Frequency Domain) and Bioheat Transfer modules on COMSOL were used to simulate the electromagnetic distribution and heating effect in the system. The localized heating of the magnetic particles due to high frequency electromagnetic waves and the subsequent increase in the temperature makes the cancer cells more susceptible to conventional therapeutic procedures. This leads to effective cell apoptosis.

The approach proposed can be used in the near future for developing novel classes of therapeutic devices for the treatment of adenocarcinoma.

SESSION SM01.06: Poster Session: Materials for Biological and Medical Applications

Wednesday Afternoon, April 24, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E
Oxidative stress during sepsis pathogenesis remains the most important factor creating imbalance and dysregulation in immune-cell function, usually observed following initial infection. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), a potentially toxic reactive oxygen species (ROS), is excessively produced by pro-inflammatory immune cells during the initial phases of sepsis and plays a dominant role in regulating the pathways associated with systemic inflammatory immune activation. In the present study, we constructed a peroxide scavenger manganese-soluted polymeric albumin manganese dioxide (mSPAM) nanoassembly to catalyze the decomposition of H\textsubscript{2}O\textsubscript{2} responsible for the hyper-activation of pro-inflammatory immune cells. In a detailed manner, we investigated the role of mSPAM nanoassembly in modulating the expression and secretion of pro-inflammatory markers elevated in bacterial lipopolysaccharide (LPS)-mediated endotoxemia during sepsis. Through a facile one-step solution-phase approach, hydrophilic bovine serum albumin reduced manganese dioxide (BM) nanoparticles were synthesized and subsequently self-assembled with cationic manganeseoslated dextridye cross-linked polyethyleneimine (mSPM) to formulate mSPAM nanoassembly. In particular, we observed that the highly stable mSPAM nanoassembly suppressed HIF1α expression by scavenging H\textsubscript{2}O\textsubscript{2} in LPS-induced macrophage cells. Initial investigation revealed that a significant reduction of free radicals by the treatment of mSPAM nanoassembly has reduced the infiltration of neutrophils and other leukocytes in a local endotoxemia animal model. Furthermore, therapeutic studies in a systemic endotoxemia model demonstrated that mSPAM treatment reduced TNF-α and IL-6 inflammatory cytokines in serum, in turn circumventing organ damage done by the inflammatory macrophages. Interestingly, we also observed that the reduction of these inflammatory cytokines by mSPAM nanoassembly further prevented IBA-1 immune-positive microglial cell activation in the brain and consequently improved the cognitive function of the animals. Altogether, the administration of mSPAM nanoassembly scavenged H\textsubscript{2}O\textsubscript{2} and suppressed HIF1α expression in LPS-stimulated macrophages and thereby inhibited the progression of local and systemic inflammation as well as neuroinflammation in an LPS-induced endotoxemia model. This mSPAM nanoassembly system could serve as a potent anti-inflammatory agent, and we further anticipate its successful application in treating various inflammation-related diseases.

**SM01.06.02 Magnetic Field-Inducible Drug-Eluting Nanoparticles for Image-Guided Thermo-Chemotherapy**

In Kye Park, Yong Yeon Jeong, Myeong Ju Moon, Sang-Joon Lee, and Yong-Kyu Lee; 1Department of Biomedical Sciences, Chonnam National University, Hwasun, Korea (the Republic of); 2Department of Radiology, Chonnam National University Medical School, Hwasun, Korea (the Republic of); 3Department of Health Administration, Gwangju Health University, Gwangju, Korea (the Republic of); 4Department of Green Bioengineering, Korea National University of Transportation, Chungju, Korea (the Republic of).

Multifunctional nanoparticles integrating cancer imaging and treatment modalities into a single platform are recognized as a promising approach; however, their development currently remains a challenge. In this paper, we synthesized magnetic field–inducing drug-eluting nanoparticles (MIDENs) by embedding superparamagnetic iron oxide nanoparticles (Fe\textsubscript{3}O\textsubscript{4}; SPIONs) and cancer therapeutic drugs (doxorubicin; DOX) in a temperature-responsive poly (lactic-co-glycolic acid) (PLGA) nanomatrix. Application of an external alternating magnetic field (AMF) generated heat above 42 °C and subsequent transition of the PLGA polymer matrix (Γ = 42–45 °C) from the glassy to the rubbery state, facilitating the controlled release of the loaded DOX, ultimately allowing for simultaneous hyperthermia and local heat-triggered chemotherapy for efficient dual cancer treatment. The average size of the synthesized MIDENs was 127.1 ± 3.20 nm in diameter. In vitro studies showed that the MIDENs were cytocompatible and especially effective in destroying CT26 colon cancer cells with AMF application. In vivo studies revealed that the MIDENs enabled enhanced T-contrast magnetic resonance imaging and a significant suppression of malignant tumor growth under an AMF. Our multifunctional MIDENs, composed of biocompatible substances and therapeutic/imaging modalities, will be greatly beneficial for cancer image-guided thermo-chemotherapy applications.

**SM01.06.03 Design and Fabrication of a Piezoelectric Microcantilever Sensor for Measurement of Cardiomyocyte and Skeletal Muscle Force Generation**

Elizabeth Colín, Alisha Colon, Christopher J. Long, Narasimhan Siram Narasimhan, and James H. Hickman; 1NanoScience Technology Center, University of Central Florida, Orlando, Florida, United States; 2Hesperos, Inc., Orlando, Florida, United States.

Piezoelectric materials have the ability to convert mechanical energy to an electrical signal leading to their use in a variety of microscale sensor systems having biological and medical applications such as pressure sensors, chemical sensors, and biosensors. Additionally, the ability of piezoelectric materials to convert electrical signals to mechanical energy has led to their use as microactuators. Microcantilever sensors have been increasingly used in biomedical microelectromechanical systems (bioMEMS) to measure small scale mechanical movement. One application is in the determination of contractile force of various muscle tissues using in vitro human-on-a-chip systems, which have typically used imaging methods or optical laser deflection of cantilevers for calculating contractility. Incorporation of piezoelectric materials into cantilever-based mechanical sensors would enable a direct electrical readout during muscle contraction. Moreover, these cantilevers could be used in reverse, as actuators, to impose a stress on tissues attached to the device. This work describes the design and fabrication of a piezoelectric biosensor cantilever which can act as either a sensing element for tissue contraction or as an actuator to apply mechanical force to cells. A piezoelectric sensing element composed of a thin film of aluminum nitride (AlN) was fabricated on a micromachined silicon cantilever which was subsequently integrated with human primary skeletal muscle or human iPSC-derived cardiac muscle to monitor the contractility of the muscle tissues. An electrical signal generated by the piezoelectric element from the contracting muscle (skeletal or cardiac) was interfaced to a commercial amplifier for recordings. Force generation was calculated from cantilever deflection data generated by spontaneous or stimulated contraction of the cells. The ability of the piezoelectric cantilevers to serve as actuators for applying mechanical stress to tissue constructs was evaluated using an optical beam displacement measurement method to detect the deflection of the piezoelectric cantilever under a periodic waveform of applied voltage. This novel bioMEMS sensor has the potential for incorporation into human-on-a-chip systems for basic physiological investigation and pharmaceutical compound development, cosmetics toxicity testing, and personalized medicine.

**SM01.06.04 Synthesis and Characterization of Biopolymer-Capped Mesoporous Silica Nanomaterials for Drug Delivery**

Cecilia Kinang, Brian Trevyn; 1Chemistry, University of St. Thomas, St. Paul, Minnesota, United States; 2Chemistry, Colorado School of Mines, Golden, Colorado, United States.

Mesoporous silica nanoparticles are an extensively studied material in drug delivery because of its porous nature, stability, and biocompatibility. In this research, MCM-41 type mesoporous silica was studied for use as controlled drug release into the oral cavity. This was achieved through loading of the model dye toluidine blue into the pores of MCM-41 and coating the loaded particles with starch. The starch is digested by the salivary enzyme, α-amylase, allowing for controlled release into the oral cavity. After optimizing the dye loading procedure, the enzymatically mediated dye release of the starch coated particles was monitored over a three-hour period in the presence of and absence of α-amylase. The dye release rate increased in the presence of α-amylase, indicating the efficacy of these materials for enzymatically triggered drug release into the oral cavity.

**SM01.06.05 Specific Interaction of Lactose Modified Graphene Oxide by the Hepatic Asialoglycoprotein Receptor**

Kevin Diaz-Galvez, Erika Silva-Campa, Alexel Burgara-Estrella, Martin Pedroza-Montero, and Jose A. Sarabia-Sainz; Universidad de Sonora, Hermosillo, Mexico.

We describe the evaluation of lactose modified graphene oxide (GO-LA) as potential drug carrier targeted to hepatic asialoglycoprotein receptor (ASGPR). Structural-modification and functional analysis of GO-LA were performed. The structure and morphology of the composite were analyzed by scanning electron microscopy (SEM), and atomic force microscopy (AFM), while Raman spectroscopy was used to track the chemical modification. For the safe application of GO-LA an evaluation of the cytotoxic effect and specific interaction of glycoconjugate were also studied. The SEM and AFM analysis of the GO showed graphene sheets with 2-3 nm layer size and few of them reached the 4 nm. Raman spectrum showed the characteristic peaks of graphene oxide at 1608 cm\textsuperscript{-1} and 1350 cm\textsuperscript{-1} corresponding to G and D bands, respectively. Null cytotoxic effects were observed for GO samples proving the biocompatibility. The biorecognition of GO-LA and the specific absorption to HepG2 cells were confirmed. The high efficacy of conjugation, hemolytic safety, and specific recognition described here lactose modified GO represents a potential drug delivery vehicle to hepatic tissue.

**SM01.06.06 Smart Chitosan Nanoparticles and Their Capacity as a Drug Delivery System**

Alexel J. Burgara-Estrella, Jorge L. Loya-Duarte, Jose A. Sarabia-Sainz, Erika Silva-Campa, Martin Pedroza-Montero and Daniel Fernandez-Quiroz; Universidad de Sonora, Hermosillo, Mexico.

Cancer is one of the leading causes of death around the world. The lifestyle and external factors can increase the cancer risk, no matters economical status and develop of countries. Current therapies such as radiation and chemotherapy alone or in combination are still unsatisfactory, and survival of cancer patients is still low. Therefore, it is necessary to develop a novel therapy that improves survival rates and the quality of life for cancer patients. In this sense, smart nanocarriers constitute an evolving possibility for controlled drug delivery to the tumor, which minimizes side effects in the patient. Among its properties, these systems have the option to respond reversibly to external factors, such as temperature, pH, ionic strength, and others. The chitosan-graft-poly(N-vinylcaprolactam) (CS-g-PVCL) is a water-soluble copolymer that could comply with requirements for
SM01.06.10
Bioconvertible and Biodegradable Polystyrene Nanoparticles for Brain Tumor Targeting

Rui Xiong, Shengtao Yu, Shuaidi Zhang, Volodymyr F Korolovych and Vladimir V. Chonnam National University Medical School, Jeollanam-do, Korea (the Republic of); 2The University of Akron, Akron, Ohio, United States; 3University of Illinois at Chicago, Chicago, Illinois, United States; 4University of Akron, Akron, Ohio, United States; 5Beijing University of Chemical Technology, Beijing, China.

In this study, a novel approach to block a carboketone (CB)-based zwitterionic segment in polyurethanes (PU) to address biocompatibility, anti-fouling properties and tunable mechanical properties has been developed. This zwitterionic PU was synthesized with CB-based diol and CB-based triol, respectively. The hydrolysis of both diol and triol segments at the interface generates zwitterionic CB functional groups that provide excellent anti-fouling properties via the enhanced hydration capacities of CB groups. This thermostimuli-responsive nanoparticle can be utilized for drug delivery and gene therapy applications. Owing to its biocompatibility, thermal stability, tunable mechanical properties and good anti-fouling properties, this CB-based polyurethane can be emerged as a promising candidate for biomedical application. It also can be an alternative replacement for those PUs without anti-fouling properties.
The development of nanoparticles which can be used as a stimuli responsive drug carrier for the treatment of different diseases has been an emerging area of research interest. In our study, we have designed a chitosan-bilirubin micelle (nanoBil) carrying losartan for the treatment of liver fibrosis which is responsive to intrinsic reactive oxygen species (ROS). Bilirubin is hydrosoluble in nature and its carboxyl group was conjugated to the chitosan amine group using the EDC-NHS chemistry to form amphilic conjugate nanoBil. Losartan has proved to be an angiotensin I receptor blocker having hepatic fibrosis reduction capability and it is being used as the therapeutic payload in this study to form nanoBil-losartan micelle. The ROS responsive Nano micelle can release loaded drug inside at the liver fibrotic area, hence liver fibrosis is characterized with high ROS levels.

The release characteristic of nanoBil-losartan was tested by ROS generator to confirm losartan release. The reduction in the hepatic stellate cell activation after the treatment of nanoBil-losartan were analyzed based on the alpha smooth muscle actin (α-sma) expression both in vitro (LX2 cell line) and in vivo studies. Hydroxyproline level as well as histopathological evaluation of the liver showed a decreased collagen content in the treated groups. Both the intravenous and intraperitoneal administration of the nanoBil-losartan resulted in a decreased level of fibrosis in thioacetamide (TAA)/Ethanol induced liver fibrosis C57H6 mouse model. The in vivo and in vitro results suggest that the ROS stimuli responsive nanoBil nanoparticle could be a potent therapeutic option for inflammatory diseases like liver fibrosis which are abundant of ROS.

SM01.06.13 Unexpected Electroanalytical Activity of the Stainless 304 Needle Toward Blood Glucose Determination [Ha]oon Lee, Hong Chul Lim, Pham S. Nguyen, Young-hun Seo, Ji-young Lee, Truong Kha Phu Cuong and Ik-Soo Shin; Soongsil University, Seoul, Korea (the Republic of).

Accurate and precision are essential requirements for chemical analysis. Herein, we developed highly precise amperometric sensor for point-of-care diagnosis of blood glucose. Stainless steel 304 needle was employed as a sensing electrode since it possesses decent electrical properties with low material cost. Especially, we found that it displayed extremely low non-faradaic background current in electrochemical condition as well as highly precise and sensitive current response specifically toward hydrogen peroxide. In blood condition, we confirmed the stainless steel 304 needle immobilized with glucose oxidase showed current signal at -0.15 V (vs SCE) upon the addition of glucose. The amperometric current signal from the modified electrode was highly specific to the blood glucose with negligible response towards interfering species. Moreover, the signal from the glucose was extremely precise with linear correlation in the diabetic blood sugar concentration range of 1-20 mM (y = 2.52328 x 10^3, R² = 0.9952) with negligible standard deviation (σ = 1.78 x 10^-3, n = 5, CV = 0.10 – 0.84 %). These results demonstrate that stainless steel 304 needle electrode hold great potential in electroanalytical biosensors based on redox enzymes relevant to hydrogen peroxide.

SM01.06.14 Excessive Metalloenzymes Condensed DNA Nanoparticles for Tumor Targeted and Drug Delivery [Li]in, Haoran Zhao and Leilei Tian; Sothern University of Science and Technology, Shenzhen, China.

Abstract: As a new and hot spot, the nucleic acid nanotechnology plays a more and more important role in cancer targeted therapy because of its perfect biocompatibility, high sensitivity and functional richness. Including directional drug carrier and release, fluorescent tracking and so on. DNA condensation is a good way to get these kind of carriers. Metal complexes, such as Co(NH3)2, can induce DNA condensation. A recent study found that pyrophosphate magnesium, the RCA reaction by-product, can condense the long single stranded DNA into the tight micro structure. Based on this finding, we report a condensation of single-strand DNA with excessive magnesium ions and form the nanoparticles whose diameter is around 100nm. Furthermore, combined with the programmability of DNA sequence and structure, we finally get an functional Mg-DNA nanoparticle with high doxorubicin loading rate, high tumor-targeting property, high biocompatibility and low toxicity. Due to the wealth of DNA sequence design, this kind of DNA nanoparticles will have a great potential on nano-medical treatment in the future.

Keywords: DNA condensation, tumor-targeted chemotherapy, nanomaterial, drug delivery

Reference:

SM01.06.15 Physico-Chemical Effects of Gelatin Addition in Carboxymethylcellulose and Calcium Phosphate Cement-Based Nanocomposites [Eesa] Guban and Daygu Ege; Bogazici University, Istanbul, Turkey.

Nanocomposites comprising of biopolymers and calcium phosphate cements (CaP) are promising due to their biocompatibility, non-toxicity, biodegradability and suitable mechanical properties for biomedical applications. In here, a new composite material was synthesized with carboxymethylcellulose (CMC) and gelatin (GEL) as the liquid phase and CaP based powder as the solid phase. In this study, the effect of the addition of different wt% of GEL including 0, 5, 10, 20 in the liquid phase was investigated on the physical properties of the nanocomposites. Physico-chemical characteristics of materials were determined by using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and mechanical tests. Swelling analysis was performed after 1, 8, 16, 24 and 48 hours and the degradation of samples was studied after 7 and 14 days. FTIR results showed that there was a physical interaction between CMC and GEL with H bonding which was evident from the peak at 3288cm⁻¹. Disruption in GEL structure was observed from the band at 1600-1400 cm⁻¹. Disruption of GEL structure may increase the interaction between CMC and GEL molecules. After mixing of solid and liquid phases, negative charges on CMC and Ca²⁺ molecules start to interact with each other and produce attraction sites for PO₄⁻ molecules. This lead to an accumulation of hydroxyapatite-like structures. A homogenous and porous microstructure was observed by using SEM in all samples. Mechanical tests showed that GEL improved the strength of the samples up to 20 wt% of GEL. The addition of 20 wt% of GEL decreased the mechanical properties. The compressive strength values were found up to approximately 6 MPa. Swelling results revealed that increasing in GEL concentration cause decrease in swelling until the 16th hour after that 10wt% GEL samples had the lowest swelling which was approximately 28%. Finally, degradation studies indicated that the highest degradation rate was for 10% GEL incorporated samples. Addition of further GEL also reduced the degradation rate. Overall, the addition of GEL improved physical properties of the samples for potential biomedical applications.

SM01.06.16 Enhanced Water Dispersible Carbon Nitride Nanodots Using PE Gylation—Application for Bioimaging Probes [Sing]hee Park, Sungjin Park, Dawoon Jang and Sujin Seok; Inha University, Incheon, Korea (the Republic of).

The PEGylated OCN (PEG-OCN) was well dispersed in water as nanodots with a lateral dimension showed strong photoluminescence in the visible region. Recently, thin 2D materials, such as graphene derivatives, have become an emerging nanosized platform in various biomedical applications, such as biosensors and their unique fluorescent, electronic, and morphological features, and high surface areas. In particular, graphitic carbon nitride (g-C₃N₄), composed of trizaine or tri-s-triazine building blocks containing alternating sp³-hybrid carbon and nitrogen atoms, is a stable metal-free 3D layered material. However, this γ-C₃N₄ has a less water dispersibility because stable 2D tri-s-triazine network. So we first make oxidized carbon nitride(OCN) material by using KMn0₄ in the presence of H₂SO₄. Thus 3D OCN has an oxygen abundant structure. Fluorescent materials are being used for the optical/fluorescence imaging of living cells and animal models. As such, the development of heavy-metal-free, water dispersible, and bio compatible imaging probes is still important. Carbon nitride (g-C₃N₄) is used as a bioimaging probe due to its suitable optical properties, thus enhancing its biocompatibility and dispersibility in aqueous media is required.

In this study, we incorporated short-chain polyethylene glycol (PEG) groups onto a carbon nitride network by the simple N-alkylation of hexaethylene glycolic mesylate with nuclophilic nitrogen atoms on oxidized carbon nitride. Cell-viability testing confirmed that these “heavy-metal-free” organic nanodots were highly biocompatible and noncytotoxic. In particular, the developed nanodots could provide clear confocal images of RAW 264.7 cells without weakening cell activity and displaying any aggregation in a range of concentrations (25-100 mg/mL) with bright-green emission in the cytoplasm.
Microbial carbohydrates have a variety of characteristics and original functionalities comparing with carbohydrates produced by animals and plants. Microbial carbohydrates are natural, non-toxic, biodegradable and biocompatible polymers, GRAS(Generally Regarded As Safe) and their structural diversities lead to a variety of functions. Recently, many novel applications have been developed using microbial polysaccharides such as drug delivery systems, hydrogels, nanoparticles, and materials for tablet-processing press in the pharmaceutical and biomedical industries as well as in the bio-nano engineering. Microbial polysaccharides can be utilized as stabilizer, emulsifier, thickener, gelling agent in food industries. The Microbial Carbide Resource Bank (MCRB) was established to investigate and collect various functional polysaccharides and microorganisms in order to widely utilize the microbial resources. MCRB also take a role as resource bank through microbial modification and offering a storage facility for various microbial carbohydrates and microorganisms. In addition, MCRB will contribute the properties of graphene oxide incorporated calcium phosphate cement-based injectable bone substitutes Ozan Durukan and Dogu Yetis; Bogazici University, Istanbul, Turkey.

Improving the mechanical properties of calcium phosphate cement (CPC)-based injectable bone substitutes (IBS) is crucial to expand their application in the treatment of bone defect. In this study, the effect of graphene oxide (GO) on the mechanical properties of CPC-based injectable bone substitutes (IBS) were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), rheological measurement techniques. Also, the produced IBS samples were analyzed by means of setting time and temperature, injectability, bioactivity and biocompatibility studies. To this end, IBS samples were prepared with 0.5, 1.0, 1.5 and 2.0 wt% GO incorporation. According to the results of the DMA analysis, incorporation of GO increased the compressive modulus of IBS samples after setting of the cement phase. For example, while the compressive modulus of 0.5wt% GO incorporated IBS samples was ~0.2 MPa, the compressive modulus of 2wt% GO incorporated IBS samples was ~0.7 MPa. A sharp increase of the storage modulus (G') and viscosity (Pa.s) in rheological measurement was observed which indicates the gelation temperature and gelation time. The gelation temperature and time were decreased effectively with the addition of GO. XRD analysis of GO incorporated IBS samples showed that the peak intensity and the grain size of CPC increased with respect to wt% of GO incorporation. SEM analysis of GO incorporated samples showed that all the prepared samples were biocompatible. Although the increase of wt% of GO reduced the injectability, overall, the addition of GO as a reinforcement has a positive effect on the mechanical properties and handling of injectable bone substitutes.

SM01.06.18
Investigation of the Mechanical and Rheological Properties of Graphene Oxide Incorporated Calcium Phosphate Cement-Based Injectable Bone Substitutes Ozan Demir Oğuz and Dogu Yetis; Bogazici University, Istanbul, Turkey.

Physical Properties of Calcium Phosphate (CaP) Cement-Based Nanocomposites Reinforced with Carboxylated Multi-Walled Carbon Nanotube (f-MWCNT) Sule Yets and Duygu Ege; Bogazici University, Istanbul, Turkey.

In this study, the effect of addition of 0, 0.5, 1, and 2 weight (wt) % of carboxylated multi-walled carbon nanotube (f-MWCNT) was investigated on the physical properties of calcium phosphate cement (CPC)-based injectable bone substitutes (IBS) and their structural diversities lead to a variety of functions. Recently, many novel applications have been developed using microbial polysaccharides such as drug delivery systems, hydrogels, nanoparticles, and materials for tablet-processing press in the pharmaceutical and biomedical engineering. Microbial polysaccharides can be utilized as stabilizer, emulsifier, thickener, gelling agent in food industries. The Microbial Carbide Resource Bank (MCRB) was established to investigate and collect various functional polysaccharides and microorganisms in order to widely utilize the microbial resources. MCRB also take a role as resource bank through microbial modification and offering a storage facility for various microbial carbohydrates and microorganisms. In addition, MCRB will contribute the properties of graphene oxide incorporated calcium phosphate cement-based injectable bone substitutes Ozan Durukan and Dogu Yetis; Bogazici University, Istanbul, Turkey.

Improving the mechanical properties of calcium phosphate cement (CPC)-based injectable bone substitutes (IBS) is crucial to expand their application in the treatment of bone defect. In this study, the effect of graphene oxide (GO) on the mechanical properties of CPC-based injectable bone substitutes (IBS) were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), rheological measurement techniques. Also, the produced IBS samples were analyzed by means of setting time and temperature, injectability, bioactivity and biocompatibility studies. To this end, IBS samples were prepared with 0.5, 1.0, 1.5 and 2.0 wt% GO incorporation. According to the results of the DMA analysis, incorporation of GO increased the compressive modulus of IBS samples after setting of the cement phase. For example, while the compressive modulus of 0.5wt% GO incorporated IBS samples was ~0.2 MPa, the compressive modulus of 2wt% GO incorporated IBS samples was ~0.7 MPa. A sharp increase of the storage modulus (G') and viscosity (Pa.s) in rheological measurement was observed which indicates the gelation temperature and gelation time. The gelation temperature and time were decreased effectively with the addition of GO. XRD analysis of GO incorporated IBS samples showed that the peak intensity and the grain size of CPC increased with respect to wt% of GO incorporation. SEM analysis of GO incorporated samples showed that all the prepared samples were biocompatible. Although the increase of wt% of GO reduced the injectability, overall, the addition of GO as a reinforcement has a positive effect on the mechanical properties and handling of injectable bone substitutes.

SM01.06.19
Investigating the Mechanical and Rheological Properties of Graphene Oxide Incorporated Calcium Phosphate Cement-Based Injectable Bone Substitutes Ozan Demir Oğuz and Dogu Yetis; Bogazici University, Istanbul, Turkey.

SM01.06.20

SM01.06.21


Bioprinting of autologous tissues encompasses many different steps and accelerating the procedure can be very critical for patients with an urgent need of organs. The physical aspects of self-assembly and the dynamics of multicellular systems used with printing technologies for tissue fabrication are therefore very important. We have developed a microscopic and mathematical model to study tissue fusion, an essential element of self-assembly phenomena during tissue maturation in the post-bioprinting procedure. Here, the model is generalized for different bioink geometries. A mathematical model is introduced and microscopic interactions at the cellular level in the maturation of bioprinted tissues have been studied. The fusion of tissue-like cell aggregates (cellular bioinks) is elaborated with the help of bonds among their adhesion molecules. The model is used to describe the fusion procedure. Consequently, the system energy and self-assembly force are calculated and compared in order to understand the effect of bioink geometries on the acceleration of the maturation of bioprinted tissues. Based on our microscopic and mathematical model, we introduce some topological criteria for bioinks for faster maturation of bioprinted tissues.

SM01.06.22

A Disposable Electrocatalytic Sensor for Whole Blood NADH Monitoring Hi Gyu Moon, Sung-Hoon Yoon, Ju Kyung Lee and Kyuhong Lee; National Center for Efficacy
Nicotinamide adenine dinucleotide (NADH) play a major role in enhancing in metabolic redox reactions and cellular energy metabolism in living cells. This compound with Nicotinamide adenine dinucleotide (NADH) is key central charge carriers in living cells and are essential in energy metabolism, reductive biosynthesis, and antioxidation. Therefore, the monitoring of NADH in living animals and cells still remains challenging because commercial methods including fluorescence spectra and electrochemical methods have invasive, time consuming, low sensitivity and complex. Herein we developed a one-step monitoring method for NADH via an electrocatalytic reaction using a surface-modified screen-printed electrode (SPE) for forming a self-assembled monolayer (SAM) with high stability. As a result, this electrode has a limit of detection (LOD) of 0.25 µM and a sensitivity of 0.0057 ± 0.0011 µM/µA in pure PBS and a 0.49 µM LOD with a sensitivity of 0.0076 ± 0.0002 µM/µA in cell culture medium. In particular, the applicability of this NADH sensor was shown for the first time in cell viability monitoring via NADH sensing in cell culture supernatants and inflammatory and fibrotic responses by PHMG-poly(hexamethylene guanidine phosphate) via NADH sensing in mouse blood.

SM01.06.23
Hierarchical Structured Zinc Oxide Nanowires—Polyacrylucid Microfibers Composite for Cancer Immunotherapy

Sang Won Byun1, Bumchul Park1, Prashant Sharma2, 1, Jei Beom Shin1, Jae-Won Lee2, 1, Na-Yoon Jang2, 2, Yu Jin Kim3, 1, Yumi Kim-4, 1, Nam-Hyuk Cho2, 1, 5 and Young Keun Kim-1, 1; 1Materials Science and Engineering, Korea University, Seoul, Korea (the Republic of); 2Biomedical Sciences, Seoul National University, Seoul, Korea (the Republic of); 3Biological Sciences, Seoul National University, Seoul, Korea (the Republic of); 4Research Center for Nanomaterials, Korea University, Seoul, Korea (the Republic of); 5Institute of Endemic Disease, Seoul National University Medical Research Center and Bundang Hospital, Seoul, Korea (the Republic of).

Zinc Oxide (ZnO) nanocomposites have attracted much attention for various biomedical applications, such as drug delivery, bio-sensor, diagnosis and therapy due to biocompatibility and multifunctionality. [1] Therefore, various synthesis methods of this promising material have been extensively studied to control nanostructures. [2] However, there are limitations to synthesize nanostructures by combining ZnO with other polymeric substances, especially fiber structured polymer. Herein, we introduce a unique method for synthesizing ZnO nanowires (NWs) on polyacrylic acid (PLA) microfiber and applied them for cancer therapy. The Hierarchical structured composite nanowire (NWs) and PLA microfibers are synthesized by two simple and effective methods. First, randomly oriented PLA microfibers containing ZnO nanoparticles seeds are electrospun on collector. Subsequently, ZnO NWs are directly grown from the seeds embedded in fiber via hydrothermal method. In addition, the NWs are stably fixed on the fibers and their densities are also successfully controlled according to the amount of seeds. Since the process of growing ZnO NWs from the seeds inside the fiber is a quite unique phenomenon, their growth mechanism and kinetics are also addressed in this paper. Moreover, this inorganic-organic nanocomposite provides a new approach to immunotherapy because there biodegradable, biocompatible and multifunctional properties. Conventionally, in therapy application, ZnO-based composites are directly injected into target cells to release embedded drugs or operate therapy using cytotoxicity. However, this nanocomposite plays a role in transferring only antigens on the nanowires to the cells. We demonstrated the nanocomposites induce immune response against specific target biomarkers and inhibit tumor growth in vivo. ZnO and PLA nanocomposite reduced immune suppressive regulatory T cells and improved the infiltration of T cells into tumor tissues when compared to mice immunized with PLA fibers coated with the antigen. This novel structured nanocomposite provides a new possibility in immunotherapy

Reference


SM01.06.24
Shape Dependent Magnetic Resonance Imaging Performance and Drug Release Behavior of Iron Oxide Nanoparticles

Bibek Thapa1, 2, Daysi Diaz-Diestra1, 2, Angela Luis-Matos1, 2, Juan Beltran-Huara1, Wojciech M. Jadwisienczak1, Brad R. Weiner2, 2 and Gerardo Morelli1, 2; 1University of Puerto Rico, San Juan, Puerto Rico, United States; 2Molecular Sciences Research Center, San Juan, Puerto Rico, United States; 3University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States; 4Ohio University, Athens, Ohio, United States.

Iron oxide nanoparticle (IONs)-based magnetic resonance imaging (MRI) T2 contrast agents (CAs) are broadly designed based on the size of the IONs as governed by quantum mechanical outer sphere theory. In other words, the MRI T2-weighted contrast enhancement efficacy of IONs are generally evaluated based on the size of the IONs and hence, the magnitude of their induced magnetization. Along with this pervasive design strategy, it is worthwhile to study the contrast enhancement efficacy of IONs based on their shape and could be an intriguing strategy to design high-performance MRI CAs. Here, we report the synthesis of silane-PEG grafted spherical, hexagonal and cubic iron oxide nanoparticles (Si-PEG-SIONs, Si-PEG-HIONs, and Si-PEG-CIONs) with comparable size ranging from 12 to 14 nm and their comparative study of magnetic resonance contrast enhancement performances. Our result shows that the Si-PEG-CIONs, Si-PEG-HIONs, and Si-PEG-SIONs exhibit the respective transverse relaxivity (r2) values of 64.6, 428 and 251 mM−1s−1 which are seven, four and three times than that of clinical MRI contrast agent, resovist. Further, we also studied shape dependent drug release behavior of doxorubicin (Dox)-loaded such nanoparticles in breast cancer cells (MDA-MB-231), and our study shows that the Dox-loaded Si-PEG-SIONs release Dox more rapidly than other IONs in intracellular region of the cells which is accompanied by micropinocytosis. Our results are suggestive of shape-based design consideration of iron oxide nanoparticles for non-invasive cancer imaging and controlled release drug delivery platform.

SM01.06.25
Cavitation Bubbles in Biological Soft Materials

Womwo Kang and Marc Raphael; Naval Research Laboratory, Washington District, Columbia, United States.

Soft gels that mimic properties of biological samples are increasingly utilized as tissue simulants for the assessment of potential damage, e.g., blunt injuries, to a human body against rapid mechanical inputs. As a result, capabilities to accurately characterize and predict transient, dynamic response of soft materials under fast loading rate conditions have become critical for such biomedical applications. Here we present (1) a new experimental method for characterizing dynamic cavitation nucleation in biologically relevant soft materials; (2) quantitative characterization on the critical acceleration that corresponds to the onset of cavitation dynamic; (3) pressure gradient and transient bubble dynamics due to mechanical impact. Utilizing a drop tower based system, we have quantified the critical acceleration in soft gels while concurrently visualizing material deformation during cavitation events. Our experiments show that the critical acceleration increases with increasing concentration of gels. Note that gel stiffness increases with increasing concentration. For stiffer gels, more energy is needed for local deformation of a gel associated with bubble expansion and, as a result, larger mechanical inputs, i.e., higher cavitation events. Our experiments show that the critical acceleration in the gel is proportional to the square of the depth of the sample. Our study on how biological soft materials respond to rapid mechanical inputs is an important step to understanding possible underlying injury mechanism(s) in blunt trauma and cavitation-induced brain injury.

SM01.06.26
Carbon Doping Mediated Active Trap Centres Formation in Porous Alumina for Ion Beam Dosimetry

Sangita Bhowmick1, Saptarshi Pal1, Dip Das1, Vinip K. Singh1, Saif A. Khan1, Sudipto Roybarman1, Dinakar Kanjilal2 and Alok Kanjilal1; 1Shiv Nadar University, Greater Noida, India; 2Material Science, Inter-University Accelerator Centre, New Delhi, India; 3Physics, UGC-DAE Consortium for Scientific Research, Indore, India.

In recent days, one of the major threats for human society is cancer. Hadron therapy in this context is taking attention for targeted cancer and tumor treatment though precise online dose monitoring is an important issue for safety purpose. For hadron therapy, recently carbon ion beam with high linear energy transfer is found to be more effective than the photon beams and to measure the accurate dose delivered to the patient, however, extremely sensitive thermoluminescent/optically stimulated luminescence (TLD/OSL) phosphors are prerequisite. Among several known TL/OSL oxides phosphors, carbon (C)-doped alumina (Al2O3) is favorable for radiation dosimetry, especially in medical field due to its tissue equivalent in terms of radiation absorption, high sensitivity, and simple glow curve. A facile approach to improve thermoluminescence sensitivity of electrochemically anodized porous Al2O3 (AAO) is presented by introducing C ions for ion beam dosimetry. Here, ion implantation technique has been employed for C doping in AAO in a controlled manner. HAADF-STEM, EDS mapping, and SEM studies reveal the evolution of a porous structure followed by the carbon distribution up to a depth of ~200 nm. However, the evolution of optically active F centers of increasing ion fluence has been examined by photoluminescence investigation at room temperature and TL measurement while the chemical nature of such defect centres has been extracted by depth dependent XPS analysis. Here, we will discuss such experimental results in the framework of oxygen vacancy formation, suggesting the substitution of Al2+ ions with C+ in the vicinity of oxygen vacancies as evidenced by X-ray photoelectron spectroscopy (XPS). Further, depth dependent XPS analysis reveals that in addition to the formation of F centers, a fraction of implanted carbon atoms is involved in making conducting channels which eventually
give a differential charging phenomenon at C 1s core level.

SM01.06.27
Two-Tiered Platform for Sequence-Specific Identification of Nucleic Acid Biomarkers in Complex Biological Fluids

Mashari N. Alangari1, Jovana Veselinovic1, Yuanhui Li1, Juan M. Artes2, Erkin Seke1, Joshua Hihath and Zimple Matharu1; University of California, Davis, Davis, California, United States; 2University of Massachusetts Lowell, Lowell, Massachusetts, United States.

The recent advances in point-of-care diagnostics have led to the development of high-performance electrical sensors that can provide fast measurements with low cost and multiplexing capabilities. However, detection in complex environments is still challenging due to the non-specific adsorption of proteins that may foul the sensor surface leading to signal attenuation. Therefore, nucleic acid purification from biological samples is often a crucial, yet a laborious initial step. In general, a simple and reliable approach for base mismatch detection is yet to be achieved. To address these challenges, we present an approach for a biosensor that consists of two stages for mismatch detection in complex environment with simple purification process occurs in the first stage then the second stage investigates at a molecular level the target’s sequence using single molecule break junction (SMBJ) technique. The first stage forms a nanostructured electrode, where the electrode morphology has been demonstrated to be biofouling resilient. This coating enables both detection of specific targets in a complex biological sample and their subsequent purification using electrochemical methods. The morphology of the electrodes allows small molecules to pass and participate in the bio-electrochemical reaction happening at the electrode surface. Nanoporous gold (np-Au) electrodes can be modified with a DNA capture probe which enables sensitive detection and capture of complementary DNA or RNA targets in the presence of complex media (blood). The surface-bound DNA:DNA or RNA:DNA can then be released by electrochemically cleaving the thiol-gold linkage, eluting the hybrids from nanoporous matrix for further analysis. Complementary to the electrochemical screening approach, single molecule conductance measurements can provide a molecular insight that is unavailable using electrochemical methods. The single-molecule break junction (SMBJ) system employs a movable, nanostructured electrode tip which makes direct contact to a gold substrate. In these measurements, charge transports between the electrodes through a single bridged-molecule. The magnitude of the current passing through the molecule will change drastically compared to tunneling gap. Here, the eluted sample from the first stage can be investigated using SMBJ which can differentiate between perfectly matched vs mutated targets (3-base mismatch). Our results show the difference in conductance values between perfect and mismatch targets in complex media. The advantages of combining these two approaches offer the ability of detection of single-nucleotide polymorphisms, simultaneous identification of multiple targets, high signal-to-noise ratio and low limits of detection.

SM01.06.28
Biomedical Applications for Conducting Polymers—Modulating Axonal Outgrowth via Template-Free Nano-Engineered Surfaces

Anthony M. Kisucky, Martin Autensteiner and Mohammed R. Abidian; University of Houston, Houston, Texas, United States.

Injuries involving the peripheral nervous system (i.e. nerve lesions or transaction) are estimated to count for 2.8% of all trauma cases in the United States; when considered alongside neurodegenerative disorders such as Parkinson’s disease, nerve damage has affected no fewer than 20 million people in the US alone. At present, the “gold standard” clinical intervention is a nerve autograft, which addresses the worst morbidities of nerve injury but is not without drawbacks. Autografts are limited in their ability to repair complex injuries, they often introduce new sensory deficits or neuropathy in the donor region, and may present problems with structural mismatch between donor and repaired nerve fascicles. Artificial nerve conduits are of great interest as a replacement or supplement to autograft-based techniques, but functional recovery remains an issue with current conduit designs. Incorporation of biocompatible Conducting Polymers (CPs) has been proposed to improve neurite guidance and improve conduit performance due to CPs’ electrical, physical, and chemical properties. The roughness of CP surfaces may have an important influence on the rate and directionality of axonal regeneration, but few works have specifically addressed this potential effect.

We have investigated two common biocompatible CPs, poly(pyrrrole) (Ppy) and poly(3,4-ethylenedioxythiophene) (PEDOT), fabricated using galvanostatic (GSTAT) and potentiostatic (PSTAT) methods, and characterized the surface roughness of these two polymers. While Ppy is well-known for its electrical conductivity and physical stability, PEDOT displays superior chemical stability and electrical conductivity, making it an ideal candidate for artificial conduits.

Electrodeposition was performed on microfabricated gold electrodes using a solution of EDOT or Py monomer and poly(styrenesulfonate) under GSTAT (0.1 to 1.5 mA/cm²) or PSTAT (0.5 to 0.95 V) deposition modes over intervals ranging from 1 to 10 minutes. Each surface was analyzed with materials confocal microscopy (MCM) to measure the CP film thickness and surface roughness. Additionally, the impedance and charge storage capacity (CSC) of the films were measured with impedance spectroscopy and cyclic voltammetry, respectively. Our results suggest a dual dependence of all measured properties (roughness, thickness, impedance, and CSC) on both deposition time and applied charge. For example Ppy/GSTAT films on Michigan neural electrodes, roughness (Rq) increased from 2.14±0.25nm to 12.0±0.84nm; CSC also increased from 5.7mC/cm² to 98.7mC/cm²; finally, impedance at 1000Hz decreased from 1.84±5 Ω to 3.83±4 [MRA1] [KAM2]Ω. These measurements were taken from films deposited at 1min, 0.1mA/cm² and 10min, 1.5mA/cm² respectively. Ppy properties exhibited generally linear trends, and PEDOT properties tended to display nonlinear trends. Dorsal root ganglion (DRG) cells will be cultured on these CP films and neurite outgrowth will then be assessed as a function of surface roughness. These results can be leveraged to improve the control of regenerating axons via surface cues.

SM01.06.29
Effect of Insertion of Trimetaphosphate Nanoparticles in Nylon 6,6 Nanofibrous for Dental Applications

Francisco N. Souza Neto1, Danilo M. dos Santos2, Thayse Y. Hosida1, Thamires P. Cavazana1, Leonardo A. de Moraí1, Elisabete Frohlin1, Sergio P. Campana Filho2, Emerson Rodrigues de Camargo2 and Alberto C. Delben1; 1Department of Pediatric Dentistry and Public Health, State University of Sao Paulo, Aracatuba, Brazil; 2Department of Chemistry, University of Sao Paulo, Sao Carlos, Brazil; 3Department of Chemistry, Federal University of Sao Carlos, Sao Carlos, Brazil.

The use of nanocomposite materials can contribute significantly to improve the quality of population life. In this context, nylon 6,6 (N6) is one of the most important engineering plastics in the automobile industry and has been investigated as a bone tissue scaffold. Trisodium trimetaphosphate (STMP) can be used as potential candidates for dental applications due to the anticytotoxic action of STMP when present in a bio-compatible scaffold as N6. Therefore, the present study focuses on the incorporation of STMP in N6 polymeric matrix and was evaluated and correlated to the physiochemical properties of nanocomposites. STMP nanocomposites were prepared by mechanical milling for 48h. N6 and its nanocomposites were prepared by electrospinning technique, and the N6/STMP nanocomposites were processed by adding 2.5, 5 and 10% w/w (STMP:N6). The milling process reduced the particle size of the STMP powders without affecting its crystalline structure. Particle size was reduced of micrometric to nanometric scale after mechanical milling producing particles with ~70 nm and spherical morphology. The phase structure was analyzed by FTIR technique and nuclear magnetic resonance spectroscopies employing 13C-CPTOSS (cross polarization with total sideband suppression). 13C NMR all chemical shifts were well resolved and were assigned according to N6. By FTIR spectra it was observed characteristics peaks of N6 and STMP, showing that, STMP was incorporated in N6. The morphology it was analyzed by Scanning Electron Microscopy (SEM) technique. SEM images showed the formation of nanofibers in N6 and its nanocomposites with ~150 nm of thickness for N6 and thickness higher for N6-STMP nanocomposite, showing the existence of STMP homogeneously distributed over the nanofibers. The thermal behavior was analyzed by TGA and DSC technique. Thermogravimetry analyses demonstrated improved thermal stability of N6-STMP nanocomposites with higher STMP concentration according to its barrier effect. Additionally, the increase in the glass transition temperature in N6-STMP nanocomposites indicated the reduction of polymeric chains mobility. The mechanical properties were evaluated, and N6-STMP -2.5% nanocomposite presented higher elastic modulus, elongation at rupture and tensile strength, presenting as a potential candidate in dentistry. These findings showed a new approach to add STMP nanocomposites by electrospinning in a polymeric matrix, forming stable nanofibers with potential application in dental biomaterials. With this methodology, it was possible using this methodology to insert the STMP nanocomposites in a polymeric matrix and increase the physiochemical properties of the nanocomposites formed.

SM01.06.30
 Branched Gold Nanoparticles in Anti-Bacterial Applications

Dazhong Fang1, Yujia Wang2, Linlin Sun2 and Thomas Webster3; 1Lexington Christian Academy, Lexington, Kentucky, United States; 2Massachusetts General Hospital, Boston, Massachusetts, United States.

Gold nanoparticles have been studied extensively for the strong capability in cancer treatment and their potential in the anti-bacterial field. Due to the ease of synthesis, chemical stability, and controllable toxicity, gold nanomaterials, especially branched gold nanomaterials, have attracted enormous interest as new biomaterials. This research focuses on the controlled synthesis of branched gold nanoparticles and their antibacterial applications. The surfactantless synthesis method reported by Xie and Wang was utilized to produce the 10 nm level branched gold nanoparticles. The 20 nm to 60 nm level branched gold nanoparticles were studied extensively for the strong capability in cancer treatment and their potential in the anti-bacterial field. Due to the ease of synthesis, chemical stability, and controllable toxicity, gold nanomaterials, especially branched gold nanomaterials, have attracted enormous interest as new biomaterials. This research focuses on the controlled synthesis of branched gold nanoparticles and their antibacterial applications.
nanoparticles were prepared by seed-mediated synthetic route. To investigate the anti-bacterial effects, the branch number and length were modulated by the pH value and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer concentration. Then, the branched gold nanoparticles were characterized by Ultraviolet-visible spectroscopy (UV-Vis) and transmission electron microscopy (TEM). Moreover, the 10 nm to 60 nm level spherical gold nanoparticles were produced by the method reported by Brown and Natan and utilized as the control group. Furthermore, branched nanoparticles with diverse sizes have been utilized to reduce bacterial growth (e.g., Staphylococcus aureus, Staphylococcus epidermidis, methicillin-resistant Staphylococcus aureus, and Streptococcus) for the anti-bacterial applications.

Reference

**SM01.06.31 Bioresorbable Magnesium Screw Degradation in Goats and In Vitro**

**Walter D. Tarr**

Materials Science and Engineering, University of Florida, Gainesville, Florida, United States.

Bioresorbable magnesium alloys can be used as orthopedic medical devices to provide strength during healing and degrade once healing has completed. Magnesium alloys degrade in bodily fluids and produce hydrogen gas which is removed through a body’s natural mechanisms. This study used four goats over 12 months and Hank’s solution in vitro to show the degradation rate of the alpha-275 extruded magnesium alloy. It was found that degradation rate of extruded magnesium screws is significantly slower than as-cast magnesium alloys, while hydrogen gas evolution rates were high enough to cause relatively large hydrogen gas voids inside the femur of the goat. Hydrogen gas gets removed where the screw is exposed outside the bone, but gets trapped inside the marrow region. Magnesium alloy screw show evidence of promoting calcification while hydrogen gas voids provide a scaffolding for which bone grows around. Additionally, geometry of the screw affects the degradation rate and, depending on the contact location with the bone, changes the degradation rate at that region as well. Magnesium alloy screw degradation rates were lower than expected over a year and hydrogen evolution rates were significantly higher than expected.

**SM01.06.32 Targeted Photodynamic Therapy with Hollow TiO\(_2\)-ZnPc-FA Nanophorenes**

**Minerva U. Robles\(^1\)\(^,\)\(^2\), Emma E. Ortiz-Islas\(^1\)\(^,\)\(^,\)\(^3\) and Alfredo A. Martinez-Morales\(^1\)\(^,\)\(^,\)\(^2\)**

\(^1\) Nanotechnology Laboratory, National Institute of Neurology and Neurosurgery, Mexico City, Mexico; \(^2\) Materials Science and Engineering Program, University of California, Riverside, Riverside, California, United States; \(^3\) College of Engineering - Center for Environmental Research and Technology, Riverside, California, United States.

TiO\(_2\) has been widely used as a photosensitizer for solar energy, hydrogen generation, removal of pollutants, and in biomedical applications such as photodynamic therapy (PDT). Despite its successful application in PDT, TiO\(_2\) does not distinguish between healthy and cancer cells, hence killing both. Modification by a targeting cancer agent may provide a more effective solution. In this work, hollow TiO\(_2\) nanophores (HTiO\(_2\)NS) are obtained by using a carbon template-mediated method and functionalized with Zinc phthalocyanine (ZnPc) and folic acid (FA) for enhancing its photocatalytic activity and increasing selectivity of cancer cells, respectively. To study the attachment of FA and ZnPc onto TiO\(_2\)NS, Fourrier-transform infrared (FTIR) spectroscopy is used to characterize the functionalization of HTiO\(_2\)NS. The crystal structure was analyzed using X-ray diffraction (XRD). Size distribution, morphology, and hollowness are characterized by transmission electron microscopy (TEM). Brunauer–Emmett–Teller (BET) was taken with \(N_2\) to measure the surface area and study surface porosity of produced HTiO\(_2\)NS. Furthermore, functionalized HTiO\(_2\)NS with ZnPc-FA are tested in vitro under UV illumination to measure the reactive oxygen species (ROS) generation with a fluorescent probe. A biological test was performed via a microculture tetrazolium assay (MTT) to measure cell death and assess the effectiveness of functionalized HTiO\(_2\)NS by ZnPc-FA. The results show that HTiO\(_2\)NS modified by ZnPc-FA can serve as a potential platform for targeted photodynamic therapy.

**SM01.06.33 Dual Sacrificial Molding—3D Printing of Dual Materials to Create 3D Microchannels with Free Hanging Geometries**

**Jason Wei Huang Goh**\(^1\)\(^,\)\(^2\) and Michinao Hashimoto\(^1\)\(^,\)\(^2\)

\(^1\) Engineering Product Development, Singapore University of Technology and Design, Singapore, Singapore; \(^2\) Digital Manufacturing and Design (DManD) Centre, Singapore University of Technology and Design, Singapore, Singapore.

We fabricated microchannels with overhang and helical geometries by sequential sacrificial molding of two substrates printed by a fused deposition modelling (FDM) 3D printer. Using a 3D model consisting of two complementary materials, we fabricated a sacrificial mold with free-hanging geometries removable in water after the removal of the other substrate used as a support material. 3D printing has become an indispensable tool to fabricate microfluidic devices. In particular, FDM 3D printing has been used to create entire microfluidic devices and to fabricate sacrificial molds in removable materials. Although 3D printing may confer wide freedom of design, the geometry of the attainable sacrificial mold is limited to the capabilities of the 3D printer and associated materials. For example, sacrificial molds made with a single material in FDM cannot offer microchannels with overhang features. 3D geometries such as dual helixes remain challenging to print using FDM printing, and requires the use of auxiliary tools to facilitate printing of geometry suspended in air.

To address these limitations, we demonstrated a method that we termed dual sacrificial molding. In dual sacrificial molding, we used two complementary materials (high impact polystyrene (HIPS) and polyvinyl alcohol (PVA)) to fabricate 3D microchannels with free hanging geometries. PVA was used to model the microchannel, and HIPS was used as a support material for the PVA mold. HIPS in the sacrificial mold was firstly removed by soaking in limonene to reveal the PVA mold harboring the free-hanging geometries. We showed that PVA was intact and retained the original design after the exposure to limonene. Thereafter, the PVA sacrificial mold was embedded in PDMS and subsequently removed by soaking in water. Using this method, we fabricated two representative designs of microchannels such as dual pyramidal networks of microchannels and dual helical microchannels, both of which were not achievable by the 3D printing of sacrificial molds based on a single material.

The capabilities of dual sacrificial molding to produce microchannels harboring free hanging geometries relies on the complementary pairing of two sacrificial materials and respective solvents used to remove them. Unlike direct printing of a sacrificial mold with a single material, our method extends the freedom of design of microchannels attainable by FDM 3D printing. We highlight the potential of using ubiquitously available FDM 3D printers and commercially available filament as sacrificial materials to fabricate complex 3D microchannels in a range of matrices relevant to chemical and biological applications. More specifically, the complementary pairing of PVA and HIPS allowed the retention of a water-soluble mold which is biocompatible and versatile to use with a wide plethora of matrix materials. To this end, we envision that the method presented here could serve as an essential method to fabricate complex vasculature in biologically relevant matrices which would be difficult to achieve with a single sacrificial material and other methods of 3D printing.

SESSION SM01.07: Materials for Biological and Medical Applications VI

Session Chair: Wonmo Kang
8:15 AM *SM01.07.01
Materials for Personalized Mechanomedicine Khalid Salarieh; Department of Chemistry, Emory University, Atlanta, Georgia, United States.

Given that dysregulation of mechanisms contributes to diseases ranging from cancer metastasis to lung disease, it is important to develop methods for measuring the molecular forces applied by cells. This is a difficult problem, as molecular forces are at the piconewton scale (1 kcal/mol ~7pN*nm). To address this issue, we have developed a suite of molecular tension probes that are engineered using PEG polymers, oligonucleotides, and proteins. Tension probes employ plasmic nanoparticles, which provide significant improvement in sensitivity. Fluorescence polarization spectroscopy and super-resolution imaging provide the highest resolution maps of cell forces. I will describe the application of these probes in the study of integrin and T cell receptor mechanobiology. Finally, I will also demonstrate applications of these materials in the area of personalized mechano-pharmacology.

8:45 AM *SM01.07.02
Shape-Changing Hydrogels as Dynamic 3D Cell Culture Environments Andrea Kasko; University of California, Los Angeles, Los Angeles, California, United States.

Engineering cell culture environments that mimic both the 3D and the dynamic nature of tissues is a major challenge in tissue engineering. Even with advanced manufacturing techniques such as 3D printing, it is difficult to produce 3D structures of soft hydrogels, which are otherwise ideal for cell culture.

Self-folding materials allow the generation of cell-friendly structures with 3D complexity across a range of length scales that are difficult to achieve with printing and lithography. Folding is induced by differential stresses generated within a flexible or elastic material. Polymeric materials, and hydrogels in particular, are well-suited for self-folding applications because they undergo pronounced volume and modulus changes in response to cell-friendly stimuli such as water, pH or temperature, to generate differential stresses within. While self-folding hydrogels have been reported, heterogeneities that lead to differential swelling must be pre-patterned into the material, and thus the shape change occurs as soon as the material is placed in a physiologically relevant environment (lacks temporal control). Furthermore, only a few examples utilizing these materials with live cells have been reported.

We have designed photodegradable hydrogels incorporating ortho-nitrobenzyl moieties that permit encapsulation or cell seeding on swollen planar films. Thin sheets are programmed to undergo a 2d to 3d shape change in response to light which induces irreversible folding of the hydrogel sheet due to differential swelling of the degraded and non-degraded regions. This bottom-up approach enables the use of simple 2d precursors to create biologically relevant 3d structures such as tubes and folded containers for cell encapsulation. Unlike other shape-changing polymer systems, such as poly(N-isopropylacrylamide), the o-NB hydrogel system requires no laminated bilayers, pH change or elevated temperatures to induce shape-change. Furthermore, photodegradation based shape-change enables external temporal control of folding that can be induced at time points of choice during cell culture.

9:15 AM SM01.07.03
Engineering of Mature Human Induced Pluripotent Stem Cell Derived Cardiomyocytes Using Substrates with Multiscale Topography Parisia Pour Shahid Saeed Abadi 1,2, Jessica Gabern 1,2, Shahed Behzadi 1,2, Michael Hill 3, Jason Tresback 4, Tiam Heydari 5, Mohammad Ejtehadi 6, Nafis Ahmed 7, Elizabeth Copley 8, Jianhui Aghavardi 8, Richard Lee 9, Omid Farokhzad 2, 10 and Morteza Mahmoudi 10; 1Department of Stem Cell and Regenerative Biology, Harvard Stem Cell Institute, Boston, Massachusetts, United States; 2Mechanical Engineering-Engineering Mechanics, Michigan Technological University, Houghton, Michigan, United States; 3Department of Physiology, Sharif University of Technology, Tehran, Iran (the Islamic Republic of); 4Center for Nanostructure Systems, Harvard University, Cambridge, Massachusetts, United States; 5Department of Physics, Sharif University of Technology, Tehran, Iran (the Islamic Republic of); 6University of California, Los Angeles, Los Angeles, California, United States; 7Department of Cardiology, Boston Children’s Hospital, Boston, Massachusetts, United States; 8Brigham and Women’s Hospital, Center for Nanomedicine and Department of Anesthesiology, Boston, Massachusetts, United States; 9Center for Nanoscale Systems, Harvard University, Cambridge, Massachusetts, United States; 10Department of Physics, Sharif University of Technology, Tehran, Iran (the Islamic Republic of); 11Women’s Hospital and Harvard Medical School, Cambridge, Massachusetts, United States.

Producing mature and functional cardiomyocytes (CMs) by in vitro differentiation of induced pluripotent stem cells (iPSCs) using only biochemical cues is challenging. To mimic the biophysical and biomechanical complexity of the native in vivo environment during the differentiation and maturation process, polydimethylsiloxane substrates with 3D topography at the micrometer and submicrometer levels are developed and used as cell culture substrates. The results show that while cylindrical patterns on the substrates resembling mature CMs enhance the maturation of iPSC derived CMs, submicrometer level topographical features derived by imprinting primary human CMs further accelerate both the differentiation and maturation processes. The resulting CMs exhibit a more mature phenotype than control groups as confirmed by quantitative polymerase chain reaction, flow cytometry, and the magnitude of beating signals and possess the shape and orientation of mature CMs in human myocardium as revealed by fluorescence microscopy.

9:30 AM SM01.07.05
Evaluation of Dedifferentiation of Carbon Quantum Dots Sourced from Chitosan on Glioma Andrea Kasko; University of California, Los Angeles, Los Angeles, California, United States.

We have designed photodegradable hydrogels incorporating ortho-nitrobenzyl moieties that permit encapsulation or cell seeding on swollen planar films. Thin sheets are programmed to undergo a 2d to 3d shape change in response to light which induces irreversible folding of the hydrogel sheet due to differential swelling of the degraded and non-degraded regions. This bottom-up approach enables the use of simple 2d precursors to create biologically relevant 3d structures such as tubes and folded containers for cell encapsulation. Unlike other shape-changing polymer systems, such as poly(N-isopropylacrylamide), the o-NB hydrogel system requires no laminated bilayers, pH change or elevated temperatures to induce shape-change. Furthermore, photodegradation based shape-change enables external temporal control of folding that can be induced at time points of choice during cell culture.

9:45 AM SM01.07.06
Oligodot Nanoparticles—A New Class of Fluorescent Nanoparticles for In Vitro and NIR In Vivo Imaging Fathemeh Ostadbashpour1, Dinabandhu Sar4, Elizabeth Copley 8, Mohammad Ejtehadi 6, Nafis Ahmed 7, Richard Lee 9, Omid Farokhzad 2, 10 and Morteza Mahmoudi 10; 1Department of Cardiology, Boston Children’s Hospital, Boston, Massachusetts, United States; 2Department of Cardiology, Boston Children’s Hospital, Boston, Massachusetts, United States; 3Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 4Bradley University, Peoria, Illinois, United States.

Biological imaging is an indispensable component of modern medicine which can shed light even on the molecular level on the biological phenotype and can be utilized for the early diagnosis of a wide gamut of deadly diseases such as cancer. Conventional imaging methods such as X-ray radiography, computed tomography (CT), and magnetic resonance are commonly used in the clinic to diagnose physiological and anatomical abnormalities. Despite their high spatial resolutions, these methods are incompetent compared with optical imaging methods as the latter offer high sensitivity, real-time screening, and intraoperative feedback while also being safe because of the lack of harmful radiation. Of importance is optical imaging in the first biological window where the interference from tissue scattering and tissue autofluorescence is minimal, leading to the enhanced depth of penetration.

In particular, the great potentials of fluorescent imaging have led to the development of organic dyes and quantum dots (QDs) with high quantum yield. However, small molecules tend to get readily cleared in a short time span making the imaging practically cumbersome. On the other hand, although QDs might address the fast-renal excretion of the small organic dyes, their toxicity due to the presence of heavy elements has always been a bottleneck slowing their development for the in vivo imaging.
Herein, we disclose for the first time the synthesis of ultrasmall nanoparticles coined as “oligodots”. The term was adopted after comprehensive mass spectroscopy analysis revealed the oligomeric nature of these nanoparticles. Their hydrothermal synthesis with slight modification in the solvent, resulted in photoluminescence tuning of the derived oligodots with green-(G-Dot) and red-(R-Dot) emitting fluorescent properties. Size exclusion chromatography, AFM and HRTEM all corroborated the formation of 1.5±0.5 nm NPs. 2D Excitation- emission contours revealed that R-Dots have an at excited at 530 nm while the G-Dots have . Detailed fluorescence spectroscopic methods such as time resolved photoluminescence spectroscopy (TRPL) and fluorescent correlation microscopy were performed to fully characterize their photophysical properties. The incubation of the NPs with murine mammary breast cancer cell (MCF-7) and fluorescent confocal imaging indicated the high performance of these nanoparticles for in vitro cell imaging. Having demonstrated their feasibility for biological studies, we carried out an in vivo study in nude mice. The G-Dot and R-Dot were injected intradermally in each of the mouse’s flanks and were imaged on IVIS instrument. Spectral unmixing was utilized where the correct localization of the oligodots was achieved indicating their multiplexing potential. Moreover, the R-Dots were injected in the tail vein and the mice were imaged at various timepoints up to 24 h . The results confirmed the feasibility of the in vivo imaging and the proper time window clearance over 3 h. Histopathological examination of the major harvested organs, revealed no sign of cytotoxicity of any kind. Considering the desirable spectroscopic properties, safety and proper pharmacokinetics, these nanoparticles can offer a new platforms as novel fluorescent imaging agents on multiple levels.

10:00 AM BREAK

10:30 AM SM01.07.07
Extracellular Matrix-Inspired Materials in Calvarial Regeneration
Justine C. Lee; UCLA Division of Plastic and Reconstructive Surgery, Los Angeles, California, United States.

Defects of the cranial skeleton occur frequently secondary to trauma, stroke, cancer, and congenital anomalies. Such defects result in significant neurological, psychological, social, and vocational burdens necessitating reconstruction. Current clinical options for reconstruction include autologous bone or alloplastic materials. However, the former is limited by tissue availability and donor site morbidity while the latter is plagued with frequent complications including extrusion of material, infection, and failure particularly in hostile wounds such as those following radiation. The limitations of both options provide the impetus for investigation in calvarial regeneration. Despite decades of research, contemporary regenerative strategies consisting of expanded stem cells and growth factor cocktails delivered by scaffolding materials have not attained clinical translation due to lack of efficacy compared to autologous bone, high cost, excessive time consumption for harvest and ex vivo progenitor cell expansion, and the untoward effects of supraphysiologic dosages of growth factors. With the increasing knowledge of the instructive capabilities of the extracellular matrix, our laboratory is primarily interested in identification of regenerative biomaterials, characterization of mechanistic interactions between materials and biology, and clinical translation of regenerative biomaterials tailored for cranialmaxillofacial defects. Our laboratory recently demonstrated the ability of an extracellular matrix-inspired material composed of nanoparticulate mineralized collagen glycosaminoglycan (MC-GAG) for regeneration of massive calvarial defects in the absence of ex vivo progenitor cell expansion or exogenous growth factor supplementation. We further showed that the mechanistic basis for MC-GAG induced osteogenic differentiation was dependent on an autogenous activation of the bone morphogenetic protein receptor (BMPR) signaling pathway via expression of a panel of BMP ligands by the osteoprogenitors themselves. Our current research interests involve: 1. Inorganic ion requirements and signaling in osteogenic differentiation induced by MC-GAG. 2. Negative regulatory pathways for osteoclastogenesis and osteoclast activation induced in progenitor cells undergoing osteogenic differentiation on MC-GAG 3. Development of Good Laboratory Practices-compliant protocol for testing the safety and performance of MC-GAG in animal cranial defect models.

11:00 AM SM01.07.08
Investigation of Calcium Oxalate Crystallization Under Microfluidic Conditions Towards the Understanding of Urolithiasis
Karol Rakotozandriny1, 2; Florence Babonneau1; Ali Abou Hassan2 and Christian Bonhomme2; Sorbonne Université, Collège de France, CNRS, Laboratoire Chimie de la Matière Condensée de Paris, Paris, France; 2Sorbonne Université, CNRS, Laboratoire Physicochimie des Electrolytes et Nanosystèmes Interfaciaux, Paris, France.

Over the past decades, the increase in kidney stone (KS) formers has raised the importance to understand the bimimeralization process responsible for urolithiasis1). Calcium oxalate (CaOx) crystallization – KS main inorganic compound2) – has largely been characterized under batch synthesis conditions that cannot be regarded as biomimetic with respect to the microscale environment in the kidney and to the urinary flow. A chemical model considering these features would provide, in fine, the biomedical community with a predictive platform for suitable and reliable diagnosis.

In this work, we used a reversible microchannel to mimic the collecting duct in the nephron where CaOx stones can form due to supersaturated levels in calcium and oxalate ions3). Within the channel, CaOx crystallization was induced under co-laminar mixing of Ca2+ and Ox− ions matching pathological concentrations – i.e. hypercalciuria and moderate hyperoxaluria. Scanning electron microscopy and Raman spectroscopy were used to support our investigations. They showed that CaOx crystals precipitate in a mixture of monohydrated whewellite (CaCO3·H2O·H2O) and dihydrated weddellite (CaC2O4·2H2O·2H2O) in the microchannel, similar to what is observed by the physicians4). In situ information on the kinetics of CaOx crystal growth could be acquired in our microfluidic system. They confirmed the effect of the hydrodynamic conditions as well as of the presence of chelating molecules on the growth kinetics and the final chemistry (phase, shape) of the formed CaOx crystals. Finally, in a trial to achieve a more complex biomimetic model (formation of KS on a Randall’s plaque), hydroxyapatite was grown in the microchannel and the CaOx crystal formation was investigated.


11:15 AM SM01.07.09
Active Delivery of Nanomedicine to Glioblastoma by Engineered Mesenchymal Stem Cell Spheroid
Yeh-Hsing Lao1; Smruti Suryaprakash1; Hyeon-Youl Cho2; Mingqiang Li3, HaYeon J1; Rachel Mintz1; Ki-Bum Lee2 and Kam Leong1-3; 1Department of Biomedical Engineering, Columbia University, New York, New York, United States; 2Department of Chemistry and Chemical Biology, Rutgers-The State University of New Jersey, Piscataway, New Jersey, United States; 3Department of Systems Biology, Columbia University Medical Center, New York, New York, United States.

Although cancer nanomedicine has been developed for decades, translation has been slow. Delivery efficiency is one of the major obstacles. To tackle this issue, we report an active delivery approach using the tumor-homing capability of mesenchymal stem cell (MSC) to boost the delivery efficiency as well as the retention of nanomedicine particularly for certain intractable cancers, such as glioblastoma (GBM), which only has limited options for treatment and the outcome remains unsatisfactory. To achieve this, we engineered MSC such that they secrete the cytotoxic protein, tumor necrosis factor-related apoptosis-inducing ligand (TRAIL). Co-delivery of TRAIL and MTX using the hybrid spheroid killed the GBM cells efficiently and specifically in vitro. In an in vivo GBM model, this hybrid spheroid approach gave nearly 100-fold improvement on micelle stability. Incorporation of DNA-templated micelle did not compromise MSC spheroid’s migration capability, and more than half of the loaded micelles were stable in the extracellular matrix part of the spheroid, which could be carried by the MSC spheroids during migration toward the GBM cells.

MSC is capable of sensing the chemotaxis generated by cancer cells because of its upregulation of the specific receptors, such as C-X-C chemokine receptor type 4 (CXCR4). By labeling the extracellular matrix part of the spheroid, which could be carried by the MSC spheroids during migration toward the GBM cells.

We further engineered the MSC to secrete the cytokine protein, tumor necrosis factor-related apoptosis-inducing ligand (TRAIL). Co-delivery of TRAIL and MTX using the hybrid spheroid killed the GBM cells efficiently and specifically in vitro. In an in vivo GBM model, this hybrid spheroid approach gave nearly 100-fold improvement on micelle retention. At three-week post-administration, 11 ± 3.2 % of the micelles remained in the tumor site when the mice treated with our MSC/micelle hybrid spheroids, while only 0.16 ± 0.03 % of the micelles was found in the tumor site when treated with the single MSC/micelle approach. Accordingly, the GBM tumor grew significantly slower when treated with our hybrid spheroids, reaching only 14% of the tumor size found in the control group at day 21, the end of the experiment. Collectively, our MSC/nanomedicine hybrid spheroid approach integrates the merits of both MSC- and nanoparticle-based therapy, enabling enhanced drug delivery to achieve a superior therapeutic efficacy in vivo.
To create the tunable interface for cell engineering, this study is focusing on how to control the surface morphology of PEM with limited conditions. First, the surface density of thiol self-assembled monolayer can be the first candidate to control the morphology of PEMs. Due to unconstrained self-assembly reaction, thiol group (such as MUA) first adsorb and cover the whole surface with lying down phase that undergoes a transition to the line-up configuration to form the complete monolayer. The contact angle shows the angle was decreased after 6 hours SAM because that lying down phase of the carboxylic acid directly on the gold surface and then gradually increasing after 24 hours and 48 hours SAM to form line-up phase. Furthermore, quartz crystal microbalance (QCM) show that different SAM density will affect the formation of the PEMs and lead to different physical characteristics from dissipation diagram. More compact SAM layers, the surface weight will be higher than the low-density film as well as the surface softness. To investigate the surface morphology, Atomic force microscopy (AFM) images showed dramatically different during 6 hrs SAM for a flat surface, 24 hrs SAM to form island surface, and 48 hrs SAM for highly compact wrinkled morphology. Besides, the ionic strength of buffer can be other factors to affect more detail condition of PEMs morphology. From QCM results, salt effect will reduce or increase the electrostatic interaction between poly(acrylic acid) and poly(lysine) that reduce or enhance the surface weight of PEM. Interestingly, the morphology of PEM can be also affected to form the dots, fibers, and wrinkle structures corresponding to the salt concentration. By controlling the density of SAM and ionic strength of the buffer, the surface morphology of PEM can be fine-tuning and utilized as the new interface for cell engineering. Fibroblast cell can be utilized as the first demonstration of this platform. By monitoring morphology, proliferation and differentiation of cells, we can know more details how the PEMs affect the cell behaviors.

SESSION SM01.08: Materials for Biological and Medical Applications VII
Session Chair: Seila Selimovic
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 229 A

2:00 PM SM01.08.02
Design of Artificial Exosomes for Cancer Diagnosis
Hojun Kim, Sungwook Park, and Kwan Hyi Lee; Department of Biomedical Engineering, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 2Department of Biomedical Engineering, Korea University of Science and Technology (UST), Daejeon, Korea (the Republic of).

Exosomes are small (few tens to hundreds nm) vesicles secreted by various cells in human body. Recent advances of nanotechnology unveiled that exosomes contain important biomarkers including miRNAs and different types of proteins specific to parent cells. Hence, increased number of studies are reported the potential of exosomes as a stable and reliable biomarker for various cancers. Previous approaches are mainly focused on utilizing heterogeneous and complex exosomes derived from human cells / body fluids. Because of the innate complexity of exosomes samples, translational research is limited and these limiting factors can be categorized into 1. Isolation, 2. Detection and 3. Heterogeneity problems. For example, gold standard isolation method requires time-consuming ultracentrifugation yet its effects on exosome morphology are not well-understood. Additionally, there are limited number of studies on differentiating cancer specific exosomes from other exosomes derived from normal cells.

In this talk, we will talk about our strategy of designing artificial exosomes through microfluidics mixer design for understanding exosome sensing with field effect transistor (FET) based biosensor device. Specifically, artificial exosomes with 40, 70, and 100 nm size with narrow size distribution (PDI = 0.01) are successfully synthesized with desired density of membrane proteins and membrane charge densities. We will discuss how exosomes’ size, charge density, and concentration of membrane proteins are correlated to sensing signals in the FET biosensor through combined small angle x-ray scattering and cryogenic transmission electron microscope techniques. Finally, we will discuss how these relations can be used to interpret sensing signals from urinary exosomes.

2:15 PM SM01.08.03
Nanocopper and Copper(II)-Based Coatings for Inhibiting Bacterial Contamination via Droplets or Touch
Debirupa Mitra, En-Tang Kang and Koon Gee Neo; National University of Singapore, Singapore, Singapore.

Bacterial surface contamination is a major cause of hospital-associated infections (HAIs), and antibacterial coatings can play an important role in reducing bacteria transmission via inanimate surfaces in healthcare settings. Coatings with nanosilver are deemed to have the potential as an antiviral surface coating for many applications such as medical devices and food packaging. Antibacterial nanosilver coatings can be easily fabricated using polydopamine (PDA) as an anchor layer to reduce and electrolessly metalize silver ions into silver nanoparticles. We have prepared nanocopper using PDA as an anchor layer, and tested its antibacterial efficacy against the nanosilver coating. In simulated contamination of inanimate surfaces by droplets or touch as expected in a hospital environment, the nanocopper coatings exhibited a much higher antibacterial efficacy than those based on nanosilver. We further investigated the relative advantages of nanocopper-PDA coatings compared to Cu(II) ion-complexed PDA coatings in terms of efficacy against the common HAIs pathogens, S. aureus and P. aeruginosa, durability as well as potential cytotoxicity. Such coatings of varying copper content were formed on poly(vinyl fluoride), latex as well as stainless steel substrates. When contaminated with droplets of the bacterial suspension, the nanocopper coating exhibited significantly higher efficacy (no viable bacteria observed after 30 min) than the Cu(II) ion-complexed PDA coatings of similar Cu content (~90% reduction in viable bacteria) due to a higher amount of Cu released by the former. However, the higher amount of Cu released by the nanocopper coating can give rise to cytotoxic effects. When contaminated with a bacteria-loaded dry surface, both surfaces were highly effective in killing the surface bacteria (no viable bacteria observed within 20-30 min). With sufficiently high copper loading (>4 μg/cm²), these Cu-containing coatings were able to maintain their antibacterial efficacy after 100 wipes with DI water. The fabrication of the Cu-containing PDA coatings can be readily scaled up for practical applications. Depending on the intended application, the Cu content as well as its physical form (ions or nanoparticle) can be selected to achieve an optimal balance between antibacterial efficacy and cytotoxicity.
that coating electrospun polyurethane vascular grafts with bioactive PEG-based hydrogel coatings confers both thrombore sistence and promotes endothelial cell attachment. However, our previous fabrication technique involved a molding process that presented significant challenges for industrial scale-up as well as difficulty in achieving thin, conformable coatings with sufficient coverage. In this study, we present a new method to assemble thin hydrogel layers on electrospun meshes through redox-initiated crosslinking mediated by the reaction between iron gluconate (IG) and ammonium persulfate (APS). We investigated IG adsorption and desorption from electrospun meshes, the effect of time on the coating thickness, and the conformability of this methodology to different geometries. Iron Gluconate Description: Bionate was electrospun onto a rotating mandrel to produce highly aligned fibers ~1 μm thick. The resultant polyurethane meshes were cut to 5x10 mm sheets, held in custom 3D-printed clamps, and soaked in 1, 3, or 5 wt% IG for 15 minutes. Meshes were then dipped in methanol and dried with compressed air. IG release from meshes immersed in water for 2 minutes in 10 second intervals was monitored with UV-Vis spectroscopy (n=18 for each concentration).

Redox Hydrogel Coatings of Tunable Thickness on Electrospun Meshes: IG-coated meshes were immersed in a solution of 10 wt% poly(ethylene glycol) diacrylate (PEGDA, 3.4kDa or 6kDa) and 0.14% APS for times ranging from 10-120 seconds. After immersion, hydrogel coated meshes were immediately immersed in water to remove excess polymer and initiator. Hydrogel thickness was measured by sectioning composites and visualizing cross sections with a stereoscope (n=12 for each condition). Conformable Coatings: To demonstrate the application of this approach for conformable coatings, tubular electrospun meshes (4 cm long, 4 mm diameter) were coated in IG and immersed in PEGDA+APS as described above. Thickness of the coatings was analyzed with a stereoscope (n=6).

IG release from meshes after 2 minutes desorbing was determined to increase from 0.06 ± 0.02 mg for a 1% IG soak to 0.46 ± 0.09 mg for a 5wt% IG soak. Hydrogel coating thickness increased from 70 ± 33 μm after a 10 second immersion in PEGDA 3.4kDa to 310 ± 66 μm after a 120 second immersion. Higher molecular weight PEGDA 6kDa coatings were 280 ± 27 μm thick as compared to 180 ± 22 μm PEGDA 3.4kDa coatings at the same time. Hydrogel coatings were formed conformably on the inside of electrospun tubular electrospun vascular grafts with a thickness of 370 ± 62 μm. In these studies, we demonstrate a tunable and scalable technique for fabricating thin and conformable hydrogel coatings on polyurethane meshes. We believe this technique can be extended to coat a range of materials with different chemistries and geometries. Coating cardiovascular devices with PEGDA hydrogel layers holds the potential to make these devices thrombore sistent and able to adhere endothelial cells. Future work will include coating artificial heart valves and individual fibers as well as assembling tough hydrogel coatings with this technique.

References:

3:00 PM BREAK

3:45 PM SM01.08.08 Persistence of Traits Acquired from Micropillar Arrays—Mechanotransduction in A549 Human Lung Adenocarcinoma

Seong Hwan Kim,1,4 Youngbin Cho2,3 Eun Hye Kim3,4 Seong Hwan Kim5, Sungsu Park6, Jennifer H. Shin7 and Jeong-O Lee1; 1Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); 2Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology (KAIST), Deajeon, Korea (the Republic of); 3Laboratory of Translational Therapeutics, Pharmacology Research Center, Drug Discovery Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Korea (the Republic of); 4Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of); 5School of Mechanical Engineering, Sungkyunkwan University, Suwon, Korea (the Republic of).

Cells are mechanically stimulated by the surrounding environment of extracellular matrices, neighboring cells and varieties of possible external physical stresses, and respond dynamically toward such mechanical stresses change of biochemical signaling pathways induced with physical stimulation has named as “Mechanotransduction”, and has a crucial effect on cell proliferation, invasion, migration, apoptosis and differentiation. Especially, cells on various artificial mechanical cues (different stiffness substrate, pillar arrays, Linea patterns) dramatically altered cell morphologies and cellular behavior. Here, A549 human lung adenocarcinoma cells were cultured on micropillar arrays made with UV-curable polymer resin (2 micrometer diameter, 16 micrometer pitch) for 48 H and intensively investigated for the understanding of mechanotransduction effect in (2.16) micropillar arrays. A549 cells grown on extremely stiff micropillar arrays (Young’s modulus of NOA 63 : 1.66 GPa) showed dramatic elongation effect in cell morphology. Confocal microscope image analysis reveals co-localization of actin filament withvimentin and relatively large number of nuclear deformation compared to A549 cells grown on flat NOA 63 substrate. Also, migration arrays in both in a single cell level (single cell tracking) and collective migration (wound healing assay, spreading assay) consistently confirm increased motility of cells grown in (2.16) micropillar assay. In vivo mouse xenograft experiment also confirms increased tumor colonization in mice injected with A549 cells grown in micropillar arrays, a character acquired from mechanical stress in-vitro even persists in in-vivo environment.

We suggest that stimulation given by the (2.16) micropillar array substrate stored in cell nucleus to be passed into next generations. The relationship between the mechanical stress given by the (2.16) micropillar arrays and mechanotransduction in A549 cells will be discussed in detail.

3:00 PM BREAK

3:30 PM SM01.08.06 Large-Scale Neural Interface Devices Dion Khodagholy; Columbia University, New York, New York, United States.

As our understanding of the brain’s physiology and pathology progresses, increasingly sophisticated technologies are required to advance discoveries in neuroscience and develop more effective approaches to treating brain disease. There is a tremendous need for advanced materials solutions at the biotic/abiotic interface to improve the spatiotemporal resolution of neuronal recording. Organic electronic devices offer a unique approach to these challenges, due to their mixed ionic/electronic conduction, mechanical flexibility, enhanced biocompatibility, and capability for drug delivery. We designed, developed, and characterized conformable organic electronic devices in the form of transistors and electrodes that efficiently interface with the brain and acquire neurophysiological activity not previously accessible with recordings from the brain surface. These devices have facilitated large-scale rodent neurophysiology experiments and uncovered a novel hippocampal-cortical oscillatory interaction. The biocompatibility of the devices allowed in-vivo recording from patients undergoing epilepsy surgery, highlighting the translational capacity of this class of neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices. In parallel, we are developing the high-speed electronics and embedded acquisition and storage systems required to make high channel count, chronic neural interface devices.

4:00 PM SM01.08.07 Delivery of siRNA Against PCSK9 Using a Thermostable Exoskeleton Increases LDL Uptake in Liver Cancer Cells In Vitro Sangeetha Swarna Lakshmi Krishnamurthy; Nihar Masurkar, Siddarth Deshpande, Samira Sadeghi and Chester Drum; NUS Medicine, Singapore, Singapore.

Hypercholesterolemia is one of the primary causes of cardiovascular disease in the developed world. A combination of genetic factors and high-fat diet causes this condition and is characterized by high LDL levels in the blood. Liver is the key organ in modulating cholesterol levels in the body and often has a lack of or overproduction of certain genes that lead to high blood cholesterol levels. Recently, loss-of-function mutations in PCSK9 gene in the liver has been shown to significantly reduce blood LDL cholesterol levels. In our study, we have encapsulated the PCSK9 siRNA into an engineered ferritin-based, C-terminal truncated, thermostable exoskeleton (tES) via charge complementation. Encapsulation was achieved by disassembly of tES at mild pH 5.5-5.8 followed by siRNA loading and cage reassembly at pH above 6 and the particles had an average size of 12 nm. The positively charged 8 nm pores of tES stably accommodate the negatively charged siRNA molecules. High loading levels of siRNA were achieved and the encapsulated biomolecules were well protected against thermal and nuclease degradation. The tES encapsulated Cy3-labelled siRNA achieved higher transfection rate than non-encapsulated and lipofectamine-delivered siRNA in HepG2 liver cancer cells as observed by fluorescence microscopy. PCSK9 knockdown in HepG2 cells resulted in significantly higher LDL uptake in vitro with a 27% increase after 60 seconds.

4:15 PM SM01.08.08 Hyaluronate–Gold Nanorod/DR5 Antibody Complex for Noninvasive Theranosis of Skin Cancer JungHo Lee and Sei Kwang Hahn; Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).
Noninvasive transdermal delivery is a promising method with distinct advantages including patient compliance over other delivery routes. Here, hyaluronate–gold nanorod/death receptor 5 antibody (HA-AuNR/DR5 Ab) complex was developed for transdermal theranostics of skin cancer. The successful formation of the complex was corroborated by 1H nuclear magnetic resonance, UV–vis spectroscopy, dynamic light scattering, zeta potential, and transmission electron microscopy. In vitro biological activity of the complex was verified by ELISA and MTT assay using HCT116 cancer cells. In addition, in vivo photoacoustic imaging and two-photon microscopy clearly visualized the transdermal delivery of HA-AuNR/DR5 Ab complex through the inevitable barrier of stratum corneum in the skin. Furthermore, in vivo antitumor effect on skin cancer model mice was confirmed from statistically significant decrease of tumor-reflecting luciferase expression levels and apoptotic signals in terminal deoxynucleotidyl transferase dUTP nick end labeling (TUNEL) assay. Taken together, we could confirm the feasibility of HA-AuNR/DR5 Ab complex as a novel theranostic platform for noninvasive transdermal treatment of skin cancers.

4:30 PM Session SM01.08.09
Non-Invasive Oral Cancer Detection from Saliva Using ZnO-rGO Nanocomposite Based Bioelectrode Shilpi Verma,1, 2 and Surinder P. Singh1, 2
1CSIR - National Physical Laboratory, New Delhi, India; 2Academy of Scientific and Innovative Research (CSIR-NPL Campus), New Delhi, India.

Oral squamous cell carcinoma (OSCC) cases are major health concerns worldwide. The early detection of the disease is expected to reduce more than 50% of mortality/morbidity rate. To this end, the point-of-care devices such as easy to use biosensors may play a significant role compared to existing techniques that are costly and need trained manpower. Realization of accurate and inexpensive biosensing systems for early detection of oral cancer demands for development of robust and multifunctional systems with excellent electron transport properties and biocompatibility. We report the synthesis of zinc oxide-reduced graphene oxide (ZnO-rGO) nanocomposite for the fabrication of electrochemical immunosensor for oral cancer biomarker 'IL8'. The detection immunosensor has been prepared by covalently immobilizing (anti-IL8) antibodies on the surface of ZnO-rGO composite thin films on ITO. The nano-immunosensor showed successful detection of IL8 at low concentration ranges i.e. 100 fg mL⁻¹ to 5 ng mL⁻¹ with very high sensitivity (12.4 µA mL ng⁻¹), selectivity and enhanced stability. These results have been validated through in-vitro investigations using real saliva samples spiked with IL8. The obtained results indicate that ZnO-rGO composite constitutes a potential biosensing test-bed for non-invasive onsite detection of oral cancer and can be upgraded into a device for clinical applications in future.

4:45 PM Session SM01.08.10
Single Stranded DNA Encapsulated Two-Dimensional Metal Dichalcogenides for Combating Multi-Drug Resistant Bacteria Abhishek Debnath1 and Alexander Green Green1, 2
1Arizona State University, Tempe, Arizona, United States; 2Biosense Institute, Arizona State University, Tempe, Arizona, United States.

Two-dimensional transition metal dichalcogenides (TMDCs) has been widely explored for wide range of biomedical applications such as delivery vector for chemotherapeutic drugs, tissue engineering and tomographic imaging. Previous reports on solution state processing of TMDCs relied on chemical based liquid phase exfoliations, which in turn provides serious challenges for its implementations in biosystems due to its hazardous nature and long processing time. To overcome these problems, we developed novel biocompatible solution state processing of TMDC in presence one of the pivotal building block of biology, single stranded DNA (ss-DNA). Extensive characterization of DNA encapsulated TMDCs using Transmission electron microscopy, High resolution transmission electron microscopy, Atomic force microscopy and optical absorbance showed successful exfoliation of TMDCs into monolayer or bilayer. Also, DNA assisted exfoliation yielded dispersed TMDCs with concentration as high as 1 mg/ml, significantly higher than previously reported biocompatible dispersing agents. Furthermore, our studies also revealed DNA assisted exfoliation of TMDCs depends on composition of TMDCs and DNA nucleobases sequence. We further demonstrate non-covalent functionalization of MoS₂surface using protein molecules with the aid of functionalized DNA and characterized using atomic force microscopy. Furthermore, we demonstrate that MoSe₂-encapsulated in ss-DNA exhibit strong bactericidal property against both gram-positive and gram-negative bacteria. Antibacterial study of MoSe₂-ssDNA showed 3.4 order higher log reductions for both gram-positive and gram-negative bacteria respectively, compared to strongest carbon based bacterical material, graphene oxide. We further tested antibacterial property of this material towards multidrug resistant bacteria, gram-negative E. coli and gram-positive MRSA, which showed 100% eradication at concentrations of 150 µg/ml and 80 µg/ml respectively. We further extended our study and eradicated 'ESKAPE' at 75 µg/ml of MoSe₂-ssDNA. Further mechanistic investigation of antibacterial activity of MoSe₂-ss DNA using Scanning electron microscopy and transmission electron microscopy, showed physical interaction of bacteria with sharp edges of nanomaterials causes breakdown of cell membrane, leading to leakage of cytoplasm and finally cell death. We further evaluated antibacterial mechanism using tools from microbiology, which showed disturbance of membrane potential coupled with development of oxidative stress as key mechanism for antibacterial actions. We anticipate incorporation of this bactericidal material into the surface coating material will eliminate multidrug resistant based nosocomial type of infections in clinical settings.

SESSION SM01.09: Materials for Biological and Medical Applications VIII
Session Chair: Wonmo Kang
Friday Morning, April 26, 2019
PCC North, 200 Level, Room 229 A

8:15 AM Session SM01.09.01
Fabrication of Vapor Crosslinked Hyaluronan-Polyethylene Interpenetrating Polymeric Network for Flexible Leaflet Heart Valve Replacements Hieu T. Bui, 1 David Prawel 1 and Susan James 2, 3 1School of Biomedical Engineering, Colorado State University, Fort Collins, Colorado, United States; 2Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado, United States; 3School of Advanced Materials Discovery, Colorado State University, Fort Collins, Colorado, United States.

Current advancement in the cardiovascular field has demonstrated that transcatheter heart valve replacement is a promising alternative to traditional heart valve replacement by open heart surgery, which is expensive and invasive. Transcatheter heart valves containing flexible leaflets made from hyaluronan enhanced linear low-density polyethylene interpenetrating polymeric network (HA-LLDPE IPN) films have been shown to be hemodynamic, but the resulting IPN surfaces were not consistent. Vapor crosslinked HA-LLDPE can improve the consistency of HA surface composition. Moreover, the novel biomaterial is resistant to enzymatic degradation and is cytotoxic. The present work describes the development of the novel HA-LLDPE fabrication process and subsequent characterization of the new materials.

The HA-LLDPE IPN formation is a multi-step process that involves swelling LLDPE film in xylene containing silylated HA-cetrimonium complex (SHACTA) to diffuse the polysaccharide into the swollen polyethylene, vapor crosslinking the SHACTA in the LLDPE to itself above a solution containing toluene diisocyanate (TDI) and xylene, and then reverting SHACTA back to HA. Treatment parameters were varied to study their effects on the IPN formation including SHACTA/xylene concentration, TDI/xylene concentration, and vapor crosslinking time and temperature. Thermal analysis helped quantify the SHACTA weight composition on treated LLDPE. Gas chromatography-mass spectrometry was implemented to determine the crosslinking vapor content. Water contact angle goniometry, infrared spectroscopy, and toluidine blue O staining were used to characterize the surface of the HA-LLDPE IPN.

Based on the collected data, TDI can effectively vapor crosslink the HA incorporated within the LLDPE, and some amount of xylenes is required during vapor crosslinking to then reverting SHACTA back to HA. Treatment parameters were varied to study their effects on the IPN formation including SHACTA/xylenes concentration, TDI/xylenes ratio, and vapor crosslinking time and temperature. Thermal analysis helped quantify the SHACTA weight composition on treated LLDPE. Gas chromatography-mass spectrometry was implemented to determine the crosslinking vapor content. Water contact angle goniometry, infrared spectroscopy, and toluidine blue O staining were used to characterize the surface of the HA-LLDPE IPN.

4:30 PM Session SM01.09.02
Application of DNA as a Programmable Molecular Glue for Bioconjugation and Assembly of Nanostructures Kurt Gothelf1, 2
1NANO and Department of Chemistry, Aarhus University, Aarhus, Denmark.

We are using DNA as a programmable tool for directing the self-assembly of molecules and materials. The unique specificity of DNA interactions and our ability to synthesize artificial functionalized DNA sequences makes it the ideal material for controlling self-assembly and chemical reactions of components attached to DNA sequences. In particular...
we are using DNA origami, large self-assembled DNA structures as a template for positioning of materials such as organic molecules, dendrimers and biomolecules. In recent years we have developed methods for conjugation of small molecules and DNA to proteins such as antibodies. The studies are now extended to the assembly of multifunctional structures and investigation of their potential as drugs. We are furthermore using combination of DNA, antibodies and other proteins for development of assays for quantification of small molecule drugs in blood.

9:00 AM SM01.09.03
A Biosensor on the Nanoscale—About the Fate of Functionalized Inorganic Nanoparticles in Living Cells Sebastian Kollenda1,2, Mathis Kopp1,2, Jasmin Wens1, Nina Schulze4,5, Chrisooulatis Papadopoulos6,7, Robert Pöthker8,9, Hemmo Meyer10,11 and Matthias Epple12,13.1 Inorganic Chemistry, University of Duisburg-Essen, Essen, Germany; 2 Centre for NanoIntegration Duisburg-Essen (CeNIDE), Essen, Germany; 3Rhine-Waal University of Applied Sciences, Kieve, Germany; 4 Imaging Centre Campus Essen (ICCE), University of Duisburg-Essen, Essen, Germany; 5 Molecular Biology I, University of Duisburg-Essen, Essen, Germany; 6 Centre of Medical Biotechnology (ZMB), University of Duisburg-Essen, Essen, Germany.

Calcium phosphate occurs naturally in bone tissue and teeth and is considered to have a good biocompatibility and a high biodegradability in biological applications. Due to these properties, nanoparticles based on calcium phosphate have become a powerful delivery system for a vast range of cargo molecules. This includes small molecules, DNA, RNA and proteins for in vitro and in vivo applications. Our recent studies on therapeutic applications based on nanoparticles showed promising results in the treatment of inflammations and derived carcinogenesis, vaccination against retroviral infections, as well as viral clearance, although the intracellular location of these nanocarriers remained uncertain yet. The aim in this project was to create a smart tool to visualize the intracellular pathway and the fate of such therapeutic nanoparticles.

The calcium phosphate nanoparticles (CaP-NPs) were synthesized according to Sokolova et al., colloidal stabilized with fluorescence labelled poly(ethylene imine) (ATTO490LS) and loaded with a fusion protein consisting of the two fluorescent units mRFP and eGFP. The particles were characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM). HeLa cells were incubated with protein-loaded nanoparticles (2 μg of fusion-protein with 30,000 cells per well) and stained with 75 nM LysoTracker™ Deep Red for 30 minutes, washed and then kept on ice to suppress the endocytic uptake until the start of the experiment. Live-cell confocal laser scanning microscopy (CLSM) was performed with a TCS SP8 system (Leica Microsystems) using a 63x/1.2 water immersion objective.

The CaP-NPs had a spherical morphology and were monodisperse with a typical diameter of 50-150 nm. The in vitro fluorescence assay confirmed a strong pH-dependency of eGFP fluorescence. At the physiological pH of 7.4, the fluorescence of both proteins is detectable. Under the conditions of an acidic pH of about 4.5-5.0 (inside a lysosome), the green fluorescence disappears due to the protonation of the chromophore of eGFP. Thus, only the red fluorescence of mRFP is detectable. Time-resolved CLSM demonstrated a successful endocytosis of protein-loaded nanoparticles into the cells, with mRFP and ATTO490LS fluorescence co-localizing with stained lysosomes. However, the fluorescence of eGFP was only detectable outside lysosomes, most likely inside of early endosomes, or at the cell membrane coming in from the outside, indicating the neutral pH at these locations. We created a smart tool to effectively visualize the intracellular pathway by using a pH-responding biosensor. This provides a versatile platform to further investigate the processing of bioactive nanocarriers inside of living cells.

REFERENCES
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ACKNOWLEDGEMENTS
The authors thank the Deutsche Forschungsgemeinschaft (DFG) for funding this project within the framework of the CRC 1093: Supramolecular Chemistry on Proteins, the ICCE for access to confocal laser scanning microscopy and Johannes Koch for technical help.

9:15 AM SM01.09.04
Rapid Disease Detection Using Variation in Hydrodynamic Flow Parameters of Erythrocytes in Non-Photolithographic Micro-Channels Manikuntala Mukhopadhyay, Sri Ganesh Subramaniam and Sunando DasGupta; Indian Institute of Technology, Kharagpur, Kharagpur, India.

Blood, is a complex non-Newtonian fluid, comprising of three major components – erythrocytes/red blood cells (RBCs), white blood cells, and platelets suspended in a watery liquid known as the plasma. The physicochemical properties of erythrocytes such as morphology, cell volume, membrane elasticity, and protein as well as lipid compositions are regarded as the principal biomarkers pertaining to different pathophysiological states. However, the onset of certain pathological conditions such as thalassemia, sickle cell anemia, hereditary stomatocytosis etc. could significantly alter the discocytic shape of the erythrocytes and their size. The clinical procedure for the detection of these diseases requires extensive laboratorial facilities, trained manpower and time. Hence, we posit that the morphological alterations of RBCs could serve as a diagnostic marker for specific diseases; utilizing the effectiveness of the micro-scale systems.

Blood samples were collected from the peripheral veins of healthy volunteers and were centrifuged to segregate the RBCs, and upon addition of a buffer, results in the formation of a stable suspension. Poikilocytic agent (viz. Triton) was added to the diluted samples to induce deformations in the erythrocytes. Poly(dimethylsiloxane) microfluidic channels of circular cross sections with diameters ranging from 100 – 500 μm, and length 40 mm, were fabricated using a novel, highly repeatable, soft lithography technique, with copper wires as the base mold. The diluted blood samples were then allowed to flow through the micro-channels at a controlled flow rate and the flow dynamics of the RBCs (both healthy and deformed) were monitored, and the local velocities were measured. Each experiment was repeated seven times. It was observed that the average flow velocities, as well as the flow patterns for the healthy discoidal shaped RBCs, were significantly different from that of the deformed RBCs. We postulate that the variations could be attributed to the difference in the amount of frictional drag experienced by the healthy and the deformed erythrocytes, and affirm that this methodology could be used for the sorting of healthy red blood cells from the diseased ones.

9:30 AM SM01.09.05
Atomically Thin Membranes with Nanoscale Pores for Dialysis Based Separations Piran Ravichandran Kidambi; Vanderbilt University, Nashville, Tennessee, United States.

Atomically thin membranes from 2D materials offer unique opportunities for molecular separations with high permeance and high selectivity. Here, we report the fabrication of fully functional centimeter scale nanoporous (<2-3nm) atomically thin graphene membranes for molecular separation applications. Our work focuses on systematically addressing key challenges that have limited progress in field i.e. a) scalable nanopore formation methods including in-situ, b) facile support casting, c) novel defect sealing methods and d) scalable manufacturing approaches. The synthesized nanoporous atomically thin membranes show higher selectivity and permeance (up to 100 times more) than state-of-the-art polymeric membranes and can be readily used for lab-scale dialysis.

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Ultrasonic Nanographene Oxide Biosensor on a Paper-Based Platform to Detect Bacterial Contamination in Water Stalin Karuppayil¹, 2, 3, Narayan C. Mishra⁴, Wei-Chen Tsai⁵, Wei-Ssu Liao⁶ and Chia-fu Chou⁷; ¹Department of Chemistry, National Taiwan University, Taipei, Taiwan; ²Institute of Physics, Academia Sinica, Taipei, Taiwan; ³International Graduate Program, Academia Sinica, Taipei, Taiwan; ⁴Department of Polymer and Process Engineering, Indian Institute of Technology Roorkee, Uttarkhand, India.

Water-borne pathogens and their associated diseases are the largest contributors for the mortality worldwide and turn out to be a global crisis cost approximately 5500 deaths per day. These pathogens are mostly generated due to poor sanitation, industrial effluents, sedimentation of rainwater and sewage sludge. We can reduce the death rate if we are able to do rapid detection of the pathogens on-site, which would be achieved by developing a simple, user-friendly, efficient and rapid on-site-detection tool, i.e., biosensor. Here, we report a novel label-free, cost-effective paper-based E. coli biosensor by screen-printing which employs nano-architected graphene oxide (GO) as fast electron-transfer flatland, deposited graphene (G) screen-printed on hydrophobic paper, and thereby the bio-recognition element, lectin Concanavalin A (ConA) was immobilized on the GO to have GO×ConA probe for bacterial sensing. Electrochemical characterization of the electrodes (G and GO) shows the fast electron-transfer with a calculated electroactive surface area deposited on graphene (G) screen-printed on hydrophobic paper, and thereby the bio-recognition element, lectin Concanavalin A (ConA) was immobilized on the GO to have GO×ConA probe for bacterial sensing. Electrochemical characterization of the electrodes (G and GO) shows the fast electron-transfer with a calculated electroactive surface area of 0.16 cm². The fabricated biosensor performance was tested by Electrochemical Impedance Spectroscopy (EIS) technique. The transfer resistance (Rt) of GO×ConA probe increased linearly with the bacterial concentration was observed in the range of 10^6-10^10 CFU mL⁻¹ with an estimated limit of detection (LOD) of ~10 CFU mL⁻¹: This indicates the ultra-sensitivity of our biosensor platform which is 100 more sensitive than previous studies with less time-consuming of 2-10 minutes per sample.

Our reported biosensor, being cost-effective, eco-friendly, rapid and ultra-sensitive for rapid detection, could be a strong candidate for point-of-care portable kits that avoids the use of expensive instruments and skilled personnel to assess water quality monitoring and diagnose the water-borne pathogens and their associated diseases.
GBM local recurrence mostly within 2 cm of the original surgical lesion makes a local treatment as the most promising way to reduce GBM recurrence rates. Carmustine (bi-chloroethyl-nitrosourea - BCNU) loaded Gliadel® disc is currently the only available FDA-approved local therapy device. It is implanted along the inner walls of the brain cavity created after maximal tumor resection. However, the efficacy is still not satisfactory because of a short effective period and non-conformity to the resection cavity. It releases most of BCNU drug within only 5-7 days.

Electrospinning is a highly versatile method for creating continuous fibers ranging from tens of nanometers to microns in diameter made of various composite materials, providing very high surface-to-volume ratio with a high porosity. Furthermore, using coaxial electrospinning, advanced features can be obtained, such as combination of different characteristics from each polymer in different layer and encapsulating drugs in the designated layer of fibers, providing multi-functionality and efficient drug loading to the resulting membrane.

The novel approach described here uses discs formed from multi-layered core-sheath membranes (‘NanoMesh’) to provide controlled and sustained drug release for long term periods, leading to excellent in vivo results in an animal model. NanoMesh discs have been implanted into rats and their in vivo efficacy has been evaluated. Membranes with core-sheath fibers encapsulating BCNU in core were produced with different sheath thickness using coaxial electrospinning. SEM images show uniform fiber formation with average diameter of ~2.2 µm (sheath of ~0.36 µm), and 2.4 µm (sheath of ~0.56 µm). Consistent long-term release with no initial BCNU burst release was observed in vitro for up to 160 days. To evaluate in vivo efficacy, F344 rats intracranially implanted with the most malignant 9L gliosarcoma cell line were examined. All control groups (with either no treatment, no core in fibers, or no drug in fibers) rats died very early, within 12-14 days. On the other hand, rats implanted with BCNU encapsulated membrane discs remained active and healthy throughout the observation period, up to 150 days after implantation (end of trial). The survival time of treated rats increased by a factor of ~13 over the control group, which represents the largest survival improvement reported to date. Brain histology using H&E staining shows no evidence of malignant cells even at Day 150. Even better results are possible by incorporating multiple anticancer drugs into fibers, leading to synergistic effects from cell-cycle specific and non-specific drugs.


11:30 AM SM01.09.11 Biodegradable Hollow Silica Capsules for Amphiphilic Transport and Sustained Delivery of Antibiotic and Anticancer Drugs Isabel Gessner, Eva Knakor and Sanjay Mathur; University of Cologne, Cologne, Germany.

Hollow mesoporous silica capsules (HMSC) have recently gained intense attention as drug delivery vehicles due to their biocompatibility, high loading capacity and sufficient stability in biological milieu. Herein we report on ellipsoid-shaped HMSC (aspect ratio ~ 2), synthesized using hematite particles as solid templates that were coated with a silica sol followed by acidic leaching of iron oxide. Gas sorption studies on HMSC revealed mesoporous pores (main pore width ~38 Å) and a high surface area of 308.8 m²/g. Cell uptake and successful internalization of as-prepared HMSC was proven by confocal microscopy using human cervical cancer (HeLa) cells. The suitability of HMSC for drug delivery applications was tested by loading antibiotic (ciprofloxacin) and anticancer (carmustine) compounds as model drugs for hydrophilic and hydrophobic therapeutics. A pH dependent drug release over several days under physiological conditions at 37°C was demonstrated (UV-vis spectroscopy) in both cases, which showed the versatility of HMSC in transporting hydrophilic as well as hydrophobic drugs. Ciprofloxacin-loaded HMSC were additionally evaluated towards gram negative (E.coli) bacteria to clearly demonstrate a complete bacterial growth inhibition over 18 hours using particle concentrations of 10 µg/ml.

SESSION SM01.10: Materials for Biological and Medical Applications
Session Chairs: Abhinav Acharya and Wonno Kang
Friday April 26, 2019
PCC North, 200 Level, Room 229 A

1:30 PM SM01.10.01 Materials for Biological and Medical Applications Sharon Gerecht; Chemical and Biomolecular Engineering, Materials Science and Engineering and the Institute for Nanobiotechnology, John Hopkins University, Baltimore, Maryland, United States.

Vascular differentiation and formation (morphogenesis) takes place in an intricate milieu. This unique microenvironment is situated throughout the body in diverse types of healthy tissues, yet it seems to activates/inhibits similar mechanisms of the microvasculature. Two parameters of this microenvironment seem critical for blood vessel growth and stabilization: (i) the extracellular matrix, which provides critical support for vascular cell adhesion, proliferation, migration, and morphogenesis, and (ii) low oxygen concentrations (hypoxia), which is a critical factor promoting vascularization during embryonic development and tumor growth. In this talk I will present our recent efforts to develop biomaterials that mimic these physicochemical cues to understand how downstream signaling pathways impact vascular fate and assembly from progenitors and pluripotent stem cells.

2:00 PM SM01.10.02 Supramolecular Hydrogels Enabling Innovations in Drug Formulation and Delivery Eric A. Appel; Stanford University, Stanford, California, United States.

Supramolecular biomaterials exploit rationally-designed non-covalent interactions to enable innovative approaches to drug formulation and delivery. For example, supramolecular interactions can be used to dynamically cross-linking polymer networks, yielding shear-thinning and self-healing hydrogels that allow for minimally invasive implantation in vivo though direct injection or catheter delivery to tissues. Herein, we discuss the preparation and application of shear-thinning, injectable hydrogels driven by non-covalent interactions between modified biopolymers (BPs) and biodegradable nanoparticle (NPs) comprised of PEG-PLA. Owing to the non-covalent interactions between PEG-PLA NPs and BPs, the hydrogels flow under applied stress and their mechanical properties recover completely within seconds when the stress is relaxed, demonstrating the shear-thinning and injectable nature of the material. The hierarchical construction of these biphase hydrogels allows for multiple therapeutic compounds to be entrapped simultaneously and delivered with identical release profiles, regardless of their chemical make-up, over user-defined timeframes ranging from days to months. These materials enable novel approaches to immunotherapy, which rely on precise release of complex mixtures of compounds, as well as long-term treatment strategies for a variety of disease targets. Overall, this presentation will demonstrate the utility of a supramolecular approach to the design of biomaterials affording unique opportunities in the formulation and controlled release of therapeutics.

2:15 PM SM01.10.03 Alloyed Upconverting Nanoparticle for Multiphoton Imaging and Lasing at Ultralow Fluences Bruce E. Cohen1, Bining Tian1, Angel Fernandez-Brañol2, Emory M. Chan3 and P. James Schuck3; 1Lawrence Berkeley National Laboratory, Berkeley, California, United States; 2Columbia University, New York, New York, United States.

Multiphoton imaging techniques that convert low energy excitation to higher energy emission are widely used to improve signal over background, reduce scatter in subsurface imaging, and limit sample photodamage. Multiphoton imaging relies on luminescent probes able to efficiently sum the energies of 2 or more incident photons, as well as lasers powerful enough for multiphoton excitation. Lanthanide-doped upconverting nanoparticles have proven to be among the most efficient multiphoton probes, but even UCNPs with optimized lanthanide dopant levels require laser intensities that may be problematic for living systems. Here, we develop protein-sized, alloyed UCNPs (aUCNPs) that can be imaged at the single particle level at laser intensities below 300 W/cm², over 300-fold lower than needed for comparably-sized doped UCNPs. Using single UCNP characterization and kinetic models of lanthanide energy transfer, we find that addition of inert epitaxial shells radically changes optimal lanthanide content from Yb3+, Er3+ -doped NaYF4, nanocrystals to fully alloyed compositions. At high levels of the emitter Er3+, these ions can adopt a second role to enhance the effective aUCNP absorption cross-section by desaturating sensitizer Yb3+ or by absorbing photons directly. Core/shell aUCNPs are brighter than comparably sized doped UCNPs at all laser intensities tested, over 4 orders of magnitude. Core/shell aUCNPs 12 nm in total diameter can be imaged with strong contrast through several millimeters of tissue in live mice using a laser intensity of just 0.1 W/cm². aUCNPs open up the possibility of using both low irradiance and low-energy excitation wavelengths for non-destructive bioimaging experiments. Additional recent work about dye-sensitized UCNP emission and UCNP-based micron-sized lasers will also be discussed.
References:
We applied this TS in plant growth and evaluated its effect on root phenotypes and stress response on plants such as Glycine max, Brassica rapa and Arabidopsis thaliana. Compared to hydroponic media, this TS provides root phenotypes in Glycine max that are significantly more similar to those observed in field soil and avoid stress response from root hypoxia.

Lastly we show how the tailorability of this new materials platform allows for the investigation of how root development is affected by soil heterogeneities, e.g., gradients in mechanical properties (“thigmotropism”) or water availability (“hydrotropism”). We expect that this new application of hydrogels will provide, through synthetic polymers and their functionalization, broad possibilities for the study of GxE interactions in root development, as well as the modeling of the rhizosphere.

4:15 PM SM01.10.08 Ligand Directed Hafnium Oxide Nanoparticles for the ‘Color’ Detection of Bone Microcracks In Vivo Using MARS Photon Counting CT Fatemeh Ostadhossein1, Chiara Lowe1, Indu Tripathi2, Lily Beng1, Mahdieh Moghishb, Aamin Raja2, Anthony Butler1 and Dipanjan Pan1; 1Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; 2University of Otago, Christchurch, Christchurch, New Zealand.

Bone as a high-performance functional material encounters various mechanical forces such as tensile, shear and periodic i.e. fatigue stresses which make it prone to the mechanical damages specially microcracks. The duality diagnosis of bone microcracks is crucial to estimate the fracture and fragility risk factors and to conduct the proper intervention. Several clinically used imaging modalities are currently being investigated for non-invasive three-dimensional assessment of bone microdamage in vivo. Among them, computed tomography (CT) imaging is an excellent candidate due to being clinically amenable and its capability to provide information on the anatomical features rapidly. However, the confounding radiographic attenuation from bone instrument make the bone damage detection difficult while the low spatial resolution of the machine does not allow detection of damage on the micrometer scale.

Nanoparticles composed of high atomic number materials can partially resolve the issues associated with strong x-ray attenuation from calcium in the conventional CT imaging machines. When combined with advances in the CT instrumentation, the best outcome is expected. Specifically, the incorporation of photon counting detectors resulted in the multispectral CT technology which enables the detection of exogenous contrast materials with minimal background from hard tissues. Depending on the various inherent K-edge of materials, they can be discriminated when applying fast voltage switching of the x-ray source. Materials whose K-edge absorption band falls in the range of peak tube potential of 80-140 kVp are especially suitable as they can bypass beam hardening effect in these practical beam energy ranges. It was indicated that the elements with Z=64-73 have the potential to enhance the x-ray contrast effectively as compared to iodine while higher Z elements would reduce the photon counts sensed by the detectors (such as Au, Bi, etc). Hf with Z=72 is an emerging radiopaque material with well-positioned K-edge energy (65.3 keV) has been rarely investigated for contrast agent in CT imaging especially K-edge imaging. Herein, we disclose for the first time the synthesis of the ligand-modified sub 5 nm HfO2 nanoparticles for the sensitive detection of bone microdamage. Furthermore, these nanoparticles were targeted to bone minerals by the introduction of an aminopolycarboxylic chelating agent. At the site of the microcracks, a fracture in hydroxyapatite, the major bone constituent, would result in the exposure of freshly charged ions due to the breakage of atomic bonds in the matrix. Hence, the nanoparticles targeted to the more concentrated minerals would ‘light up’ the microcrack site. We demonstrated that with the distinct spectral properties, HfO2 nanoparticles would show in ‘color’ the location and anatomy of the microcrack. Moreover, the sub 5 nm size of these nanoparticles makes it feasible for them to travel through the nutrient transport canals (e.g. Haversian canals, canaliculi, Volkmann’s canals, etc) in the muscle near the bone and microcrack itself. We indicated in the in vivo studies that these nanoparticles could effectively indicate the microcrack anatomy in the rat’s tibia in the spectral CT while the non-targeted control nanoparticles non-specifically accumulated in the muscle. Furthermore, intramuscular injection of the nanoparticles did not induce any adverse effects on the liver enzyme functions and more importantly histopathologically. Therefore, these ligand-directed HfO2 nanoparticles would open new avenues for the safe, non-destructive, sensitive bone microdamage detection in vivo with potential clinical translation.

4:30 PM SM01.10.09 Electrodeformation Studies of White Blood Cells Cultures Enriched with Gold Nanoparticles N. G. Hallfors1, J. Teo1, C. Joshi1, A. Orozalez1, B. Samara1, L. George1, M. N. Martin1 and Abdel F. Isakovic1; 1KUST, Abu Dhabi, United Arab Emirates; 2Cornell University, Ithaca, New York, United States; 3NYU, Abu Dhabi, United Arab Emirates.

Separation and other forms of microfluidic manipulation of white blood cells for immunology and related applications is critical for more specific diagnostics and future treatments. We report on the studies of mechanical and electrical properties of bio-hybrid of white blood cells (WBCs) intermixed with gold nanoparticles (AuNPs) through dielectrophoresis (DEP) measurements. Studies of WBCs are performed with both standard, with form, WBCs, and in gold nanoparticles (AuNPs) enriched form. DEP devices are microfabricated in the form of metal-on-glass microelectrode arrays, with the shape of the elements of DEP devices numerically modelled following broadly accepted elementary physical properties of white blood cells. Specifically, indium tin oxide (ITO) was evaporated onto glass to 150 nm thickness, then lithographically patterned and cured at 400 deg C to modify its transparency and achieve higher conductivity. Afterwards, individual DEP chips are used for the deposition of small volumes of cell-AuNP culture suspension into the DEP electrode region. Electrodes are connected to a function generator and wired to the source of an AC current, where electric field and frequency could both be controlled. Jurkat and THP-1 cell types are tested so far. We have followed hypothesis that mechanical modulus value and its possible changes are related to the cells’ activation, which is considered as relevant in some elements of body's immune response. Additional motivation for this set of experiments is the link between cancer and WBC’s deformability and other mechanical properties. Two main types of experiments are followed here. In the first, frequency sweeps are performed at a fixed voltage (10V), and the crossover frequency is measured to be 18.0+/−2.00 kHz for THP-1 cells and 77.5 +/- 4.30 kHz for Jurkat cells. In the second series of studies, elastic modulus is determined following measurements of aspect and stretch ratios, with THP-1 modulus in the range of 430 Pa, and Jurkat cells modulus at around 530 Pa. The introduction of Au NPs allows for the modification of the elastic modulus values by a factor varying from 1.5 to 4, depending on the reagents used when Au NPs are added (PEG with varied concentration, citrate, others), and depending on the concentration of Au NPs. Measurements so far indicate that at least a portion of Au NPs are absorbed into WBCs, while the rest are either close to WBC outer membrane or “free floating” in the cell culture suspension. As a potentially encouraging news, the addition of controllable amount of AuNPs doesn't negatively impact the overall deformability of WBCs, despite the modifications to the elastic modulus values. This hybrid, bio-materials centered system of white blood cells and gold nanoparticles is a subject of continued studies, and will likely serve as a precursor for better understanding of related systems of interest in biomaterials and immunology.

4:45 PM SM01.10.10 Self-Assembled Epigallocatechin Gallate-Metal Ion-Based Nanomaterials for Cancer Theranostics Yunlu Dai, University of Macau, Macau, Macao.

Cancer, the major public health issue, has become the leading cause of death in China since 2010. Traditional chemotherapy is still a leading approach in current cancer treatment to suppress tumor proliferation and prolong patient survival by eliminating or inhibiting cancer cells through antinecancer drugs. Nanomedicine has become rapidly growing area of medical research for cancer treatment, as they can efficiently carry and deliver therapeutic agents, imaging probes or biological materials to the targeted tumor sites by enhanced permeability and retention (EPR) effect. However, the safety of nanoparticles is essential for clinical application. Polyphenols, compounds found in our diet, could help prevent degenerative diseases such as cancer and cardiovascular diseases. Therefore, polyphenols based nanomaterials can be employed as excellent candidates for nanomedicine. Moreover, the polyphenols would seem to have great potential to promote the efficacy of antinecancer drugs. We constructed a self-assembled nanoplatfom with the help of interactions between polyphenols and Fe3+ ion. Epigallocatechin gallate (EGCG) and PEG polyphenols were employed as the polyphenols, and anticancer drug doxorubicin (DOX) was encapsulated in the core of the nanoparticles for cancer treatment. The size of nanoparticles could be controlled from 30 nm to 150 nm by tuning the Fe3+ ion concentration. More interestingly, the nanoplatfom can be used for in vivo fluorescence imaging with NIR dye modification and T1 magnetic resonance imagining (Fe3+), which is useful for cancer diagnosis. The nanoparticles are able to promote tumor treatment efficacy and prolong mice survival time compared with free drug alone. This theranostics nanoplatfom establishes a novel promising approach to design next generation nanoparticles for cancer treatment.
Cutting-Edge NIR Fluorescent Imaging Paradigm for Precise Manipulation of Cellular Activities and Localized Theranostics

11:00 AM

for developing novel anticancer therapeutics. The use of instructed-assembly (iA) in cellular environment to form polypharmaceuticals in-situ that not only interact with multiple proteins, but also modulate membrane dynamics and for develop polypharmaceuticals for selectively inducing death of cancer cells via multiple pathways and without inducing acquired drug resistance. We designed novel active and raft-affinitive probes consisting of an enzymatic trigger, a fluorophore, and a cholesterol. Being water soluble and as the substrate of ectophosphatase, the probes preferably and rapidly assemble in the membrane to exhibit strong fluorescence. Such cell compatible, active probes work at micromolar concentrations, require short incubation period, and achieve high resolution monitoring of nanoscale heterogeneity in live-cell membranes. In a related study, we developed a conjugate of tyrosine and cholesterol (TC), formed by enzyme catalyzed dephosphorylation of phospholipid TC (pTC). TC self-assembles selectively on or in cancer cells. Acting as polypharmaceuticals, the assemblies of TC augment lipid rafts, aggregate extrinsic cell death receptors (e.g., DR5, CD95, or TRAILR), modulate the expression of oncoproteins (e.g., Src and Akt), disrupt the dynamics of cytoskeletons (e.g., actin filaments or microtubules), induce ER stress, and increase the production of reactive oxygen species (ROS), thus resulting in cell death and preventing acquired drug resistance. Moreover, the assemblies inhibit the growth of platinum-resistant ovarian cancer tumor in a murine model. These results illustrate the use of instructed-assembly (iA) in cellular environment to form polypharmaceuticals in-situ that not only interact with multiple proteins, but also modulate membrane dynamics for developing novel anticancer therapeutics.

11:00 AM *SM02.01.02

Instructed-Assembly of Cholesterol Derivatives for Imaging and Inhibiting Cancer Cells

Huaimin Wang, Zhaoqianqi Feng and Ping Xu; Brandeis University, Waltham, Massachusetts, United States.

Acquired drug resistance remains a challenge in chemotherapy. Here we discuss enzymatic, in-situ assembling of cholesterol derivatives for acting as imaging probes for reveal membrane dynamics and for develop polypharmaceuticals for selectively inducing death of cancer cells via multiple pathways and without inducing acquired drug resistance. We designed novel active and raft-affinitive probes consisting of an enzymatic trigger, a fluorophore, and a cholesterol. Being water soluble and as the substrate of ectophosphatase, the probes preferably and rapidly assemble in the membrane to exhibit strong fluorescence. Such cell compatible, active probes work at micromolar concentrations, require short incubation period, and achieve high resolution monitoring of nanoscale heterogeneity in live-cell membranes. In a related study, we developed a conjugate of tyrosine and cholesterol (TC), formed by enzyme catalyzed dephosphorylation of phospholipid TC (pTC). TC self-assembles selectively on or in cancer cells. Acting as polypharmaceuticals, the assemblies of TC augment lipid rafts, aggregate extrinsic cell death receptors (e.g., DR5, CD95, or TRAILR), modulate the expression of oncoproteins (e.g., Src and Akt), disrupt the dynamics of cytoskeletons (e.g., actin filaments or microtubules), induce ER stress, and increase the production of reactive oxygen species (ROS), thus resulting in cell death and preventing acquired drug resistance. Moreover, the assemblies inhibit the growth of platinum-resistant ovarian cancer tumor in a murine model. These results illustrate the use of instructed-assembly (iA) in cellular environment to form polypharmaceuticals in-situ that not only interact with multiple proteins, but also modulate membrane dynamics for developing novel anticancer therapeutics.

11:30 AM *SM02.01.03

Structure and Function of Multi-Component Supramolecular Hydrogels

Itaru Hamachi; Kyoto University, Kyoto, Japan.

Soft matters exhibiting stimul-response under water-rich conditions are attractive because of their numerous potential bio-applications. My group recently makes efforts to design stimuli-responsive supramolecular hydrogels, inspired by natural living cells, an ultimately complex and intelligent soft material composed of numerous multiple components. By mimicking live cells, we hybridized our supramolecular with many synthetic and/or biological molecules bearing various structures and functions. We expected that controlling and facilitating the crosstalk between these multiple components could give biomolecule-response to the hybrid supramolecular hydrogels. One of the recent examples is self-sorted supramolecular nanofibers double network system. We firstly succeeded in in situ real-time imaging of self-sorted supramolecular nanofibers by using confocal laser scanning microscopy and super resolution imaging. Moreover, we are able to construct an adaptive hydrogel whose ecological property can be modulated in both directions by distinct two external stimuli.

References

We have developed two systems for delivering biologics into the cytosol. The first is nanoparticle-stabilized nanocapsules (NPSC), formed via assembly of arginine-functionalized gold nanoparticles (AuNP) around fatty acid nanodroplets. These systems have been used to deliver proteins and siRNA directly to the cytosol in vivo, and have been used for efficient delivery of siRNA targeting TNF-α in vivo, providing effective anti-inflammatory treatment.

Our second system uses co-engineering of nanoparticles and proteins to deliver proteins into the cytosol. This platform co-assembles arginine-functionalized AuNPs with proteins modified with a glutamate (E-tag) chain. This strategy has been applied to a wide range of proteins, and we have employed this system to co-deliver complete CRISPR machinery (Cas9 protein and guide RNA) for effective editing both in vitro and in vivo.

2:00 PM *SM02.02.02*

Controlling Vaccine Kinetics and Immunogen Presentation via Alum-Binding Antigens
Darrell Irvine; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The kinetics of antigen availability following immunization impact follicular helper T cell priming, germinal center responses, and ultimate antibody production, but clinically-relevant methods to control the duration of antigen delivery to lymph nodes in subunit vaccines are lacking. We conjugated antigens derived from the gp140 HIV envelope trimer with a phosphoserine (pSer) peptide that binds tightly to the most common clinical adjuvant, aluminum hydroxide (Alhydrogel, or alum). Site specific modification of an engineered outer domain (eOD) gp120 or stabilized SOSIP trimer immunogen with varying numbers of pSer groups allowed self-assembly of these antigens on the surfaces of alum particles to be tuned and alum-bound antigens were presented from alum particle surfaces with a defined orientation. Tight binding to alum converted alum itself into a nanoparticle delivery vehicle, as alum nanocrystals released from the injection site trafficked to lymph nodes and were taken up by antigen-specific B cells. Ultimately, a 30-fold increase in germinal center responses and antibody titer resulted from primary antibody production was observed four weeks prior to primary immunization with both pSer-eOD and pSer-SOSIP conjugates, and long-lived plasma cells in bone marrow were doubled by immunization with pSer-modified immunogens. Overall, pSer-antigen conjugates elicited significant increases in antibody titers and altered specificity of the humoral response through controlling the display of antigen on the surface of alum.

2:30 PM *SM02.02.03*

Cloaking Nanoparticles with Supramolecularly Pre-Coated Protein Corona for Targeted Drug Delivery
Ja-Hyoung Ryu; UNIST, Ulsan, Korea (the Republic of).

Nanoscopic delivery vehicles capable of encapsulating drug molecules and releasing them in response to external stimuli are of great interest due to implications in therapeutic applications. However, the stability of encapsulation with self-assembled systems is limited during blood circulation and translating nanomedicines into clinical applications still remains a challenge due to the difficulty in regulating interactions on the interfaces between nanoparticles and biological systems. Thus, deliberate molecular design for stable encapsulation, targeting and triggered release is required. For this purpose, we have developed a facile synthetic method for highly stable, polymeric nanogels or polymer-caged hollow nanoparticles using a simple inter/intra-chain crosslinking reaction. We show a simple method for the preparation of biocompatible nanovehicles that provides the ability to encapsulate hydrophobic or hydrophilic drug molecules. Nano-carriers showed great stability to encapsulate drug molecules and drugs were only released inside cell. In addition, we showed a targeting strategy for nanoparticles incorporated with a supramolecularly pre-coated recombinant fusion protein in which HER2-binding affibody combines with glutathione-S-transferase. Once thermodynamically stabilized in preferred orientations on the nanoparticles, the adsorbed fusion proteins as a corona minimize interactions with serum proteins to prevent the clearance of nanoparticles by macrophages, while ensuring systematic targeting functions in vivo. This study provides insight into the use of the supramolecularly built protein corona shield as a targeting agent through regulating the interfaces between nanoparticles and biological systems.

2:45 PM *SM02.02.04*

Enzymatic Assemblies Disrupt Membrane and Target Endoplasmic Reticulum (ER) for Selective Cancer Cell Death
Zhaoqianqi Feng, Huaimin Wang and Bing Xu; Brandeis University, Waltham, Massachusetts, United States.

Organelle targeting has emerged as a promising strategy in developing effective and specific cancer therapeutics by delivering a drug in its active form to the cellular compartment where it works. Among all the subcellular targets, endoplasmic reticulum (ER) targeting therapy has been little explored due to its complexity in cell signaling. As the largest cellular organelle, ER is responsible for crucial biosynthetic, sensing, and signaling functions in eukaryotic cells. Particularly, ER is responsible for the synthesis, folding, and posttranslational modifications of proteins destined for the secretory pathway, which amount to approximately 30% of the total proteome. Disrupting the protein-folding capacity of ER would result in ER stress, ultimately activating apoptotic signaling pathways and cell death. Therefore, selective disrupting ER function in cancer cells is a promising new strategy for antitumor therapies. However, current ER targeting small molecules, like tunicamycin and thapsigargin, lack cell selectivity and exhibit severe neurotoxicity, thus hindering their clinical applications. Therefore, it is necessary to develop novel ER targeting strategies that have high specificity against cancer cells. In this work, we employ enzyme-instructed self-assembly (EISA) to selectively target ER of cancer cells. Generated via enzymatic reactions on and in the cancer cells, the enzymatic assemblies interact with cellular membranes and disrupt plasma membrane integrity to enable the assemblies accumulate on the ER, thus inducing cancer cell death through ER stress. Utilizing enzymatic reactions and reduced diffusion of assembly, EISA enables spatiotemporal control of the generation and cellular distribution of the cytotoxic assemblies, thus providing a new strategy to regulate amyloid-like aggregates for treating cancer. This work, for the first time, demonstrates a reaction-based process for disrupting membranes in a spatiotemporally controlled manner, as well as subcellular organelle (i.e., ER) targeting, which illustrates a new concept in controlling cell fates via instructed-assembly.

3:00 PM BREAK

3:30 PM *SM02.02.05*

Semiconducting Polymer Nanoparticles for Photoacoustic Imaging and Photothermal Therapy in Second Near-Infrared Window
Yuyan Jiang and Kanyi Pu; Nanyang Technological University, Singapore, Singapore.

Near-infrared (NIR) light has been intensively exploited in biomedical applications due to its unrivaled benefits. Although most studies are focused on the first NIR (NIR-I) window (650-950 nm), there is growing interest to extend the wavelength to the longer second NIR (NIR-II) window (1000-1700 nm). As compared with NIR-I window, NIR-II light benefits from reduced photon scattering in biological tissues and higher maximum permissible exposure limit. Despite the great advantage, reported nanoagents that absorb in NIR-II window are limited, which include copper sulfide nanoparticles, gold nanorods, phosphorus phthalocyanine, etc.

Recently, semiconducting polymer nanoparticles (SPN)s composed of n-conjugated polymer backbones have emerged as a new category of optical agents. Due to the benign nature, SPNs circumvent the concern of metal-ion induced toxicity and possess size- and morphology-independent optical properties. Moreover, hardgap engineering provides a way to impart SPNs with high photothermal conversion efficiency, allowing for photoacoustic (PA) imaging and cancer photothermal therapy (PTT). However, most SPN-based materials can only be responsive to visible or NIR-I light, and few have been used for NIR-II applications.

Herein, we design and synthesize the first organic imaging agent based on SPN (SPN-II) that absorbs both NIR-I and NIR-II light and apply it for NIR-II PA imaging. The broadband absorption of SPN-II allows us to directly compare NIR-II vs NIR-I PA imaging so as to find out the advantages of NIR-II light in PA imaging. Because of the weaker background PA signals from biological tissues in NIR-II window, the signal-to-noise ratio (SNR) of SPN-II resulted PA images at 1064 nm can be 1.4-times higher than that at 750 nm when comparing at the imaging depth of 3 cm. The proof-of-concept application of NIR-II PA imaging is demonstrated in vivo imaging of brain vasculature in living rats, which showed 1.5-times higher SNR as compared with NIR-I PA imaging. Our study not only introduces the first broadband absorbing organic contrast agent that is applicable for PA imaging in both NIR-I and NIR-II windows but also reveals the advantages of NIR-II over NIR-I in PA imaging.

Furthermore, to reveal the advantages of NIR-II relative to NIR-I window in terms of cancer PTT, we also report the first organic SP-based photothermal nanoagent with the dual-peak absorption in both NIR-I and NIR-II windows. Such nanoagent consists of poly[di(3-ketopyrrolopyrrole-alt-cyclopentadiithiophene)-co-di(3-ketopyrrolopyrrole-alt-thiadiadiazole) (kpp-alt-k2d)] conjugated with polyethylene glycol. The conjugation of these two segments leads to a final polymer with the nearly identical absorbance at 808 and 1064 nm. The resulted SPNs not only allows for deep-tissue NIR-II PTT but also provides the opportunity to conduct a fair comparative study between NIR-I and NIR-II windows in order to reveal the superiority of NIR-II over NIR-I light for PTT. The proof-of-concept application of SPNs is demonstrated in tumor xenograft mouse model to validate the advantage of NIR-II window over NIR-I window for deep-tissue PTT. At last, a NIR dye is doped into SPNs to afford a fluorescent nanoagent (SPNF-A) permitting NIR fluorescence imaging guided NIR-II PTT.
Multi-drug resistant bacterial infections are responsible for 7,000,000 deaths each year worldwide, with more than 10 million deaths per year predicted by the year 2050. The majority of human bacterial infections (~80%) are associated with formation of biofilms on living tissues. Early detection of biofilms is crucial for limiting infection-based damage. Imaging these biofilms is challenging: conventional imaging agents are unable to penetrate the dense matrix of the biofilm, and many are susceptible to false positive/negative responses due to phenotypical mutations of the constituent microbes. We have engineered nanomaterials to penetrate the extracellular polymeric substance (EPS) matrix of biofilms and to intrinsically target the acid microenvironment of the biofilms. Here, we report the creation of pH-responsive nanoparticles with embedded transition metal catalysis (nanozymes) that effectively target the acid microenvironment of biofilms. These pH-switchable nanozymes generate imaging agents through bioorthogonal activation of profluorophores inside biofilms. The specificity of these nanozymes for imaging biofilms in complex biosystems was demonstrated using biofilm-mammalian cell co-culture experiments.

**3:45 PM SM02.02.06**

Ph-Responsive Nanoparticle Embedded Catalysts for Imaging of Biofilm-Associated Infections

Akash Gupta, Siddha Das, Guleen Y. Tonga, Tsukasa Mizuhara and Vincent M. Rotello; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

The subjects of this talk are multifunctional mesoporous silica nanoparticles controlled by supramolecular nanomachines and caps for imaging and drug delivery in cells and in vivo. The nanoparticles are designed to 1) trap therapeutic molecules inside of the nanocarriers, 2) carry therapeutics to the site of the disease with no leakage, 3) release a high local concentration of drugs, 4) release only on command – either autonomous or external, and 5) kill the cancer or infectious organism. The most important functionality is the ability to trap molecules in the pores and release them in response to desired specific stimuli. Two types of external stimuli will be discussed: light and oscillating magnetic fields. Activation by internal biological stimuli such as pH changes, redox potential changes, antibodies and enzymes will also be presented. Molecular machines based on molecules that undergo large amplitude motion when attached to mesoporous silica - impellers, snap-tops and valves – will be described. Derivatized azobenzene molecules, attached to the interior pore walls function as impellers that can move other molecules through the pores. Nanoparticles containing antinancer drugs in the mesopores are taken up by cancer cells, and optical stimulation of the impellers drives out the toxic molecules and kills the cells. Snap-tops with cleavable stoppers release cargo molecules when the stopper is removed from the pores. Nanoparticles containing catalase are taken up by cancer cells, and optical stimulation of the nanoparticles causes the catalase to activate and destroy peritoneal metastatic tumors that are almost invisible to naked eye. Moreover, the temperature-correlated afterglow signal of SPNs permits real-time temperature monitoring during photothermal cancer therapy in living mice. The structural versatility of SPNs enables a smart activatable afterglow probe with activated signal from the pore entrance. Nanovalves consisting of rotaxanes and pseudorotaxanes placed at pore entrances can trap and release molecules from the pores in response to stimuli. Both reusable and completely reversible nanovalves will be described. Activation of these nanodevices by the five types of stimuli in solution, in living cells, and in animal models will be discussed. Applications to treatments of cancers (including pancreatic and breast) and of intracellular infectious diseases (including tuberculosis and tularemia) will be presented.

**4:30 PM SM02.02.08**

Spatial and Temporal Control of Stimulation-Responsive Theranostic Nanomaterials Using Caged Functional DNA Molecules

Yi Lu; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Theranostic nanomaterials have shown potentials for molecular diagnostic tests and targeted therapeutic applications in modern medicine. To reach their full potentials for clinical applications, novel methods for spatial and temporal control of stimuli-responsive nanomaterials are required in order to elucidate detailed mechanisms of theranostic effects in vivo and to personalize the diagnostics and treatments in clinics. Toward this goal, we have been selecting, from a large DNA library of up to 10^{13} different sequences, functional DNA molecules, such as DNAzymes (DNA molecules with enzymatic activities) and DNA aptamers (DNA molecules that can bind targets selectively) that can bind a wide variety of targets, especially those small molecular biomarkers that antibodies have not been able to recognize [1]. When conjugated to nanomaterials such as gold nanoparticles, quantum dots, liposomes, iron oxide nanoparticles, upconversion nanoparticles and polymeric organic nanoparticles, these functional DNA molecules allow stimuli-responsive assembly or disassembly of these nanomaterials, resulting in target-dependent changes of not only optical and magnetic signals for diagnostics, but also controlled release of therapeutic drugs [2]. To realize the spatial and temporal control of these stimuli-responsive nanomaterials, we have added a caged group to the functional DNA molecules so that these DNA nanomaterials can be delivered into living cells, zebrafish and other animals until a decaging event at a specific location and a certain time is triggered [3]. Recent progress in this area will be presented.


Fluorescence is a perfect technique in the preparation and evaluation of supramolecules, in the light of its advantages including superior sensitivity, fast responsiveness, high signal to noise ratio. More importantly, it can be applied for in situ visualization of bioanalytes at the molecular level and monitoring complex biochemical processes in real time. Comparing to most traditional fluorophores which suffer severe photobleaching and aggregation-caused quenching (ACQ) problems, luminogens with aggregation-induced emission (AIEgens) provide a unique light-up fluorescent signal. They are nearly non-luminescent in the isolated state but emit strongly in the aggregate/clustered state. The AIE aggregates exhibit large absorptivity, robust luminosity, strong photobleaching resistance, no random blinking and excellent biocompatibility. Based on different AIEgens, various supramolecular systems have been fabricated and present fascinating applications in biosensing, imaging and therapeutics, such as biomolecular analysis, micro-environment sensing, organelle or cellular imaging, pathogen detection and killing, as well as multimodal imaging-guided therapies.

Selected references

9:30 AM SM02.03.03
Transition Metal Mediated Bioorthogonal Catalysis with Controlled Localization and Kinetics for Nanotheranostics
Riddha Das1, Ryan Landis1, Gulen Y. Tonga2, Premskul Puangploy1, Michael Knapp1 and Vincent M. Rotello2; 1Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Harvard University, Boston, Massachusetts, United States.

Transition metal catalysis (TMCs) can be catalyzed in a wide variety of chemical transformations, making them potential tools for bioorthogonal catalysis. We recently demonstrated that TMCs can be encapsulated in the surface monolayer of nanoparticles (NP), generating water-soluble “nanozymes”. These nanozymes demonstrate catalysis reminiscent of enzymes but can also catalyze a variety of bioorthogonal processes. We report a rational approach to control the localization and kinetics of nanozymes by fine-tuning their surface chemistry. We demonstrated intra-extracellular catalysis by surface engineering of the nanozymes. We used membrane-penetrating cationic nanoparticles for catalysis inside and ‘stealth’ zwitterionic particles to limit catalysis to outside of cancer cells. Specific localization of nanozyme activity was demonstrated through profluorophore activation. Therapeutic efficacy was demonstrated through intra- and extracellular activation of a produg. Further, we fabricated nanozymes possessing different surface hydrophobicity to regulate their interaction with a library of profluorophore substrates. We determined that nanozyme catalysis efficiency was driven by supramolecular interactions between the nanozymes and substrates. This study of nanozyme surface engineering provides the nanozymes with specific localization and tunable catalysis reminiscent of their enzyme prototypes for imaging and drug delivery.

9:30 AM SM02.03.04
Enzymatic Assembling Cholesterol for Selective Cancer Therapy and Membrane Imaging
Huaimin Wang and Bing Xu; Brandeis University, Waltham, Massachusetts, United States.

Chemotherapy resistance and toxicity are major problems facing current cancer research. Here we report that enzyme responsive cholesterol conjugates effectively and selectively kill cancer cells, including platinum-resistant ovarian cancer cells. The conjugate increases the degree of noncovalent oligomerization upon enzymatic dephosphorylation in aqueous buffer. This enzymatic conversion also results in assemblies of the cholesterol conjugate inside and outside cells and leads to cell death. Mechanistic studies suggest that the formed assemblies of the conjugates aggregate extrinsic cell death receptors (e.g., DR5, CD95, or TRAILR), modulate the expression of oncoproteins (e.g., Src and Akt), disrupt the dynamics of cytoskeletons (e.g., actin filaments or microtubules), induce ER stress, and increase the production of reactive oxygen species (ROS), thus resulting in cell death and preventing acquired drug resistance. In addition, the fluorescent labeled conjugates could directly image membrane dynamics of live cells with high spatial and temporal resolution over extended time scales and areas. Being water-soluble and as the substrate of ectophosphatase, these cell compatible probes preferentially and rapidly assemble in plasma membrane, exhibit strong fluorescence, work at micromolar concentrations, and easily achieve high resolution monitoring of nanoscale heterogeneity in membranes of live cells, the release of exosomes, and the membrane dynamics of live cells. This work not only illustrates the enzyme-instructed assembly of essential biological small molecules to treat drug-resistant cancers, but also provides a facile means to investigate membrane dynamics and heterogeneity to cellular processes.

9:45 AM BREAK

10:15 AM SM02.03.05
Supramolecular Polymer-Based Nanomedicine—High Therapeutic Performance and Negligible Long-Term Immunotoxicity
Guocan Yu; National Institute of Health, Bethesda, Maryland, United States.

Nanomedicines have achieved several breakthroughs in cancer treatment over the past decades, however their potential immunotoxicity are ignored, which results in serious adverse effects and greatly reduces the potential in clinical translation. Herein, we innovatively develop a theranostic supramolecular polymer using β-cyclodextrin as the host and camptothecin (CPT) as the guest linked by a glutathione-cleavable disulfide bond. The supramolecular polymerization remarkably increases the solubility of CPT by a factor of 232 and effectively inhibits its lactone ring opening in physiological environment, which is favorable for intravenous formulation and maintenance of the therapeutic efficacy. Supramolecular nanoparticles can be prepared through orthogonal self-assembly driven by π-π stacking interaction, host-guest complexation, and hydrogen bonds. The sophisticated nanomedicine constructed from the obtained supramolecular polymer can be specifically delivered to tumor sites and rapidly excreted from body after drug release, thus effectively avoiding systemic toxicity, especially long-term immunotoxicity. In vivo investigations demonstrate this supramolecular nanomedicine possesses superior anti-tumor performance and anti-metastasis capability. This pioneering example integrating the advantages of the dynamic nature of supramolecular chemistry and nanotechnology provides a promising platform for cancer theranostics.

10:30 AM SM02.03.06
Fluorescent Upconversion Nanoclusters for Theranostic Imaging and Photodynamic Therapy
Muthu Kumara Gnanasammandhan Jayakumar, Zhen Zhang, Xiang Zheng and Yong Zhang; National University of Singapore, Singapore, Singapore.

Fluorescent upconversion nanoparticles (UCNPs) are one of the most preferred class of nanoparticles for use in near infrared (NIR) light-based theranostics. NIR light has better tissue penetration capabilities and NIR-based imaging drastically reduces the background autofluorescence, thus becoming the ideal choice in comparison to UV/visible light which has low tissue penetration capabilities and high phototoxicity. UCNPs have the unique ability of converting NIR light to a range of UV/visible/NIR wavelengths, which could be exploited for imaging and light-based therapeutic applications. The UCNPs developed so far can only be used to perform imaging and therapy simultaneously but this is not desirable as the therapeutic process activated during imaging might cause unwanted side effects and does not offer any control over the whole process. For example, tumor imaging should be performed first to identify the location of the tumor before performing the therapeutic intervention and if the UCNPs are activated in areas other than the tumor during imaging, it would cause unwanted cell killing in normal tissues. To overcome this problem, we have designed a new UCNP-nanocluster which can be used for performing temporally separated imaging and photodynamic therapy. These nanoclusters were tested in-vitro and was shown to perform imaging and photodynamic therapy without any overlap. There was no cytotoxicity observed in cells which were used for imaging but significant cytotoxicity was observed in cells subjected to photodynamic therapy using the same nanocluster. These UCNP nanoclusters offer excellent control over theranostic applications and is foreseen to be a game-changer in this field.

10:45 AM SM02.03.07
Ultrasound Iron Oxide Nanoparticles for Imaging-Guided Drug Delivery
Jennifer Sherwood1, Megan Rich2, Mark Bolding2 and Yuping Bao1; 1University of Alabama, Tuscaloosa, Alabama, United States; 2The University of Alabama at Birmingham, Birmingham, Alabama, United States.

Imaging-guided drug delivery has recently attracted much attention in nanomedicine where imaging probes are used to indicate the delivery and distribution of the drugs. For such an application of nanostuctures, the blood circulation times and effective delivery and monitoring the drugs remain as major challenges in order to reduce toxicity and enhance
drug or diagnostic efficiency. In this presentation, we present a state of art approach to forming nanoclusters by crosslinking ultrasmall iron oxide nanoparticles with bovine serum albumin. This novel design not only maintains the T1 performance of the ultrasmall nanoparticles, but also significantly increases their blood circulation times from 15 minutes to over two hours. Our breast tumor model study also exhibited enhanced localization and retention of these nanoclusters at tumor sites for more than 24 hours. The ability of maintaining the T1 performance of the ultrasmall nanoparticles is significant, because previous studies have shown complete T1 loss or signal decrease upon polymer encapsulation. This design also shows great potential in encapsulating model drug molecules, which will greatly benefit the field of imaging-guided drug delivery.

**11:00 AM SM02.03.08**

**Employing Self-Assembly for Biomedical Imaging Applications**

*Guolin Liang*; University of Science and Technology of China, Hefei, China.

Employing the property that self-assembly of probes can enhance imaging signals, we have conducted sensitive analyses on several important biomarker-instructed self-assembly processes. 1) By rational design of a system of one enzyme (alkaline phosphatase) two substrates, for the first time, we have successfully used chemiluminescence imaging to precisely analyze the simultaneous enzyme-instructed self-assembly process. 2) Using cryo transmission electron microscopy imaging analysis, we have differentiated several nanoparticles which were obtained from different biomolecule-instructed self-assemblies at angstrom scale. 3) By designing small molecular probe (or drugs), we have conducted real time fluorescence imaging (or magnetic resonance imaging, etc) analyses on the intracellular enzyme-instructed self-assembling processes of nanoprobes (or drugs).

**11:30 AM SM02.03.09**

**A Next Generation Theranostic Supra Molecular Nano-Platform for Sustained And Enhanced Inhibition of Cancer Stem Cells**

*Fatemeh Ostadsossein, Santosh Kumar Misra* and *Dipanjan Pan*; University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Signal transducer and activator of transcription factor 3 (STAT 3) is known to be overexpressed in cancer stem cells. Poor solubility and variable drug absorption are linked to low bioavailability and decreased efficacy. Many of the drugs regulating STAT 3 expression lack aqueous solubility; hence hindering efficient bioavailability. A theranostics nanoplatform based on luminescent carbon particles decorated with cucurbit[6]uril is introduced for enhancing the solubility of niclosamide, a STAT 3 inhibitor. The host–guest chemistry between cucurbit[6]uril and niclosamide makes the delivery of the hydrophobic drug feasible while carbon nanoparticles enhance cellular internalization. Extensive physicochemical characterizations confirm successful synthesis. Subsequently, the host–guest chemistry of niclosamide and cucurbit[6]uril is studied experimentally and computationally. In vitro assessments in human breast cancer cells indicate approximately twofold enhancement in IC50 of drug. Fourier transform infrared and fluorescence imaging demonstrate efficient cellular internalization. Furthermore, the catalytic biodegradation of the nanoplatforms occur upon exposure to human myeloperoxidase in short time. In vivo studies on athymic mice with MCF 7 xenograft indicate the size of tumor in the treatment group is half of the controls after 40 d. Immunohistochemistry corroborates the downregulation of STAT 3 phosphorylation. Overall, the host–guest chemistry on nanocarbon acts as a novel arsenal for STAT 3 inhibition.

**SYMPOSIUM SM03**

Growing Next-Generation Materials with Synthetic Biology

April 24 - April 25, 2019

**Symposium Organizers**

Patrick Boyle; Ginkgo Bioworks

Mathew Chang; National University of Singapore

Rajesh Naik; Air Force Research Laboratory

Renee Wegrzyn; Defense Advanced Research Projects Agency

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**SESSION SM03.01: Synthetic Biology I**

Session Chairs: Rajesh Naik and Renee Wegrzyn

Wednesday Afternoon, April 24, 2019

PCC North, 200 Level, Room 227 B

**1:30 PM SM03.01.01**

**Genetic Encoding of Material Properties**

*Christopher Voigt*; Department of Biological Engineering, Massachusetts Institute of Technology, Boston, Massachusetts, United States.

I will describe approaches to obtain new materials from engineered cells and how genetic engineering can be applied to change the material properties. The focus will be on materials that are difficult or impossible to produce via synthetic chemistry and have unique functional properties (e.g., electrical or optical).

**2:00 PM SM03.01.02**

**Synthetic Biology Toolkits for Bacterial Cellulose Production**

*Sierin Lim, Meng How Tan* and *Vishnu Vadanan Sundaravadanam*; Nanyang Technological University, Singapore, Singapore; 2A*STAR Genome Institute of Singapore, Singapore, Singapore.

Bacterial cellulose is an exopolysaccharide produced by various species of bacteria, with *Gluconacetobacter xylinus* being the model organism to decipher the biosynthesis of cellulose. It has potential applications in food, pharmaceutical, and cosmetic industries due to its unique structure and mechanical property. The cellulose produced by bacteria is of high purity and crystallinity compared to those isolated from wood pulp due to the absence of lignin and hemicellulose. Despite the natural production capacity and the biogenesis knowledge, bacterial cellulose is produced in relatively low quantity. In this study, we systematically rewired the natural production cascade to enhance cellulose production capacity and the self-assembly of microfibers for the synthesis of tailor-made and customizable cellulose. *Gluconacetobacter xylinus* produces cellulose by converting UDP-glucose to cellulose through cellulose synthase located in the cell membrane. The gene encoding cellulose synthase is comprised of four subunits and is arranged in an operon. To study the metabolism of genetically modified cellulose synthase and how it affect cellulose production, we develop genetic tools and build a library of genetic parts in BioBrick formats. We have completed the construction of genetic toolkit library for the manipulation of three *Acetobacteraceae* family members that are *Gluconacetobacter xylinus* (ATCC 700178), *Gluconacetobacter hansenii* (ATCC 53582), *Komagataeibacter rheticus* (GEM). We further constructed plasmids carrying different combinations of the four cellulose synthase subunits and introduced them into the bacteria for expression to create a mutant library of synthetic host capable of producing cellulose with different capacity and property. In this study, we also examine the self-assembly mechanisms and microstructures of bacterial cellulose. Never-dried native bacterial cellulose produced from two *Acetobacteraceae* family members are disintegrated into individual fibres through TEMPO-mediated oxidation and mechanical treatment, obtaining transparent and viscous suspension. Although the main oxidant is NaClO, we find that mechanical treatment (ultrasonication) plays an important role in the disintegration process of the bacterial cellulose.
The morphology of the disintegrated fibrils are observed by SEM and the crystallinity of the disintegrated fibers are analysed by XRD. The organic functional group of the cellulose fibres are as characterized in dry state and wet condition by FTIR and RAMAN, respectively. The birefringence of the fibre suspension is also investigated under polarizing microscope. The oxidized cellulose fibres are expected to have physical interaction with metal ions. We will study this interaction in respect of forming conductive cellulose complexation. We further develop a method to synthesize bacterial cellulose hollow microparticles that are challenging to achieve using conventional method. The reformed cellulose have been shown to improve wound healing.

2:15 PM SM03.01.03
DNA-Based Attractor Patterns [Phillip J. Dorsey and Rebecca Schulman] 1,2; 1Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 2Computer Science, Johns Hopkins University, Baltimore, Maryland, United States.

We have developed a system for fabricating and perturbing self-healing oligonucleotide-based attractor patterns in photolithographically-patterned hydrogels using ultraviolet radiation. Digital maskless photolithography combined with microfluidic handling methods provides the ability to construct soft materials of arbitrary shape at biologically relevant length scales of tens to hundreds of microns in a matter of seconds. The photoinitiator system we incorporate with this platform enables the UV-light directed initiation of photosensitive DNA-based reactions in structured hydrogels. We use this approach to first form self-healing linear and hill-shaped DNA-based patterns in poly(ethylene-glycol) diacrylate hydrogels. Undisturbed, these spatial patterns were stable over at least 24 hours. When patterns were perturbed in particular areas they reformed their original shape. The ability to grow and perturb gradients of biomolecules such as DNA may facilitate the study of cell populations in dynamic microenvironments, providing experimentalists control over where and when chemical cues are induced or inhibited at the microscale.

2:30 PM BREAK

3:30 PM SM03.01.04
Toward Utilizing Bacterial Microcompartments as a Platform for Enhanced Catalysis [Matthew D. Yates, Jefferson Plegaria, Clement Aussignargues, Sarah Glaven and Cheryl Kerfeld] 1,2, 1U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2MSU-DOE Plant Research Laboratory, Michigan State University, East Lansing, Michigan, United States; 3Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 4Department of Plant and Microbial Biology, University of California, Berkeley, Berkeley, California, United States.

Harnessing and engineering natural biological processes to synthesize and self-assemble highly ordered materials with nanoscale components and features is key for developing the next generation of functional biomaterials. One such nanoscale material naturally synthesized by some bacteria is a self-assembling, selectively-permeable protein shell called a bacterial microcompartment (BMC). These microcompartments are used by cells to shield sensitive metabolic reactions from the intracellular environment (e.g. oxygen sensitive CO2 fixation enzymes or enzymes that produce toxic intermediates). The selectively permeable shell consists of different protein components, most with a pore at the center, which serves to concentrate reactants and increase reaction kinetics. BMCs are an attractive platform because the components of the microcompartments (the shell proteins and/or the encapsulated proteins) can be engineered, synthesized separately, and self-assembled in the absence of a living cell, providing a great deal of design space for customization. As a proof of principle, one BMC named microcompartment shell protein (the trimeric BMC-T protein) was engineered to coordinate a FeS metal cluster at the pore, which conferred reversible redox activity to the protein in solution. Further, the FeS-modified BMC-T protein also displayed reversible redox activity when it was bound to an electrode surface, with a similar formal potential (E′ = –370 mV vs SHE) to what was obtained in solution. Further, when the protein was engineered to coordinate the FeS cluster to the opposite side of the pore, multiple redox peaks with different midpoint potentials (E′ = –460 and –340 mV vs SHE) were observed. We have also observed redox activity from an electrode-bound BMC-T protein modified to coordinate a Cu metal center at the pore, with a formal potential(s) that is also dependent on the site modified to coordinate the metal center (E′ = 200 mV [site 1], 410 and 550 mV [site 2]). These results suggest that the BMC platform is a versatile architecture that can be customized to suit various applications (e.g. sensor development, electrosynthesis, and energy storage and conversion) and represent an important step toward harnessing naturally-occurring, self-assembling, nanoscale biomaterials to perform surface bound redox chemistry in a tunable, controlled environment.

3:45 PM SM03.01.05
Development of Microbial Cell Factories for Production of Aromatic Chemicals and Derivatives [Akihiko Kondo] 1,2; 1Graduate School of Science, Technology and Innovation, Kobe University, Kobe, Japan; 2Center for Sustainable Resources, RIKEN, Kanagawa, Japan.

Bio-based chemicals currently receive attention as sustainable and drop-in substitutes for petroleum-based chemicals. The feedstocks used for the production of bio-based chemicals have recently expanded from edible sugars to inedible lignocellulosic biomass. The production of bio-based chemicals is a key target of the 2030 Agenda for sustainable development. In this study, we hypothesized that the development of microbial cell factories (MCFs) will significantly contribute to the achievement of the 2030 Agenda. MCFs are engineered microorganisms that can be used to produce a wide range of chemicals from renewable feedstocks. MCFs can be engineered to produce a variety of chemicals, including aromatic chemicals and derivatives. Here, we discuss the potential of MCFs for the production of aromatic chemicals and derivatives.

Keywords: Biorefinery; Lignocellulosic biomass; metabolic engineering; synthetic biology.

References:

4:00 PM *SM03.01.06
Accessing Novel Materials Through Biology [Sanil Chandran; Amyris, Emeryville, California, United States.

Biological systems are an important source of inspiration for the development of novel materials. The process of evolution has led to the development of a wide range of materials with unique properties. In this talk, I will discuss some of the recent advances in the field of materials science using biological systems. I will also discuss the potential applications of these materials in various fields such as electronics, biotechnology, and medicine.

4:30 PM SM03.01.07
Design of Silica Structures Using Peptides from Diatoms [Andrea Wallace and Christopher Voigt; Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Development of silicon-based materials with highly organized nano- and microstructures are of increasing demand across the medical, optical, energy, and mechanical fields. Nanoscale control of silica fabrication is desirable as new functions and properties can emerge from complex structures. Current methods for controlling silica morphology often involve the use of templates or sacrificial structures, which can limit the range of possible shapes and sizes. In this talk, I will present a novel approach for designing and fabricating silica structures using peptides from diatoms as templates. The peptides are self-assembled into nanofibers, which are then used as scaffolds for silica deposition. This method allows for precise control over the morphology of the resulting silica structures, providing a new platform for the development of functional materials.
require chemical additives, extremes of temperature, pressure, or pH, and long processing times. Interestingly, biological organisms, like diatoms, naturally produce a diversity of hierarchical silica structures under ambient conditions that are difficult to obtain even through advanced synthetic methods. Here, we use the silica-mineralizing R5 peptide from the diatom *Cylindrotheca fusiformis* in combination with targeted post-translational modifications (PTMs) to rapidly synthesize silica with controlled morphology at room temperature in aqueous conditions. By screening a diverse library of modifying enzymes for activity against R5, we identified ten enzymes capable of introducing PTMs to R5 and describe a set of design rules that relate individual modifications to specific changes in silica morphology. We then use these rules to rationally design and express enzyme pathways containing multiple modifying enzymes to selectively modify R5, and demonstrate that multiple modifications create synergistic effects on silica morphology. Additionally, we show that R5 can be used in combination with synthetic and biologically produced metal nanoparticles to synthesize silica-coated core-shell nanoparticles with tunable shell thickness. This system provides a modular approach for rapidly engineering and synthesizing silica structures under ambient conditions and moves us closer to being able to synthesize complex silica structures, like those seen in nature, that will provide new functions and properties to help advance silicon-based application spaces.

**4:45 PM SM03.01.08**

**Polydopamine-Gold Nanoparticle Composite Material Synthesis by Engineered Cells**

Isaiah Weidmann and Milana C. Vasudev; University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States.

In recent years, metal nanoparticles are being used for biomedical, environmental, and industrial applications. Metallic nanoparticles, such as gold nanoparticles (AuNPs) feature prominently in plasmonics, biosensing, polydopamine and photothermal imaging. Polydopamine, which can lead to the formation of eumelanin is a biomolecule which has also gained lot of interest due to its broad absorption spectrum and has potential for optical, photo-acoustic, and biosensing applications. Formation of a biocomposite material combining such optically-active materials could lead to a tunable absorption spectrum, based on polydopamine thickness.

As the complexity of composite materials increases, the development of simple design rules become essential, and using biological building blocks is one method to achieve this. Bacterial synthesis routes offer immense potential for an efficient synthesis process, ease of functionalization, modification and repeatability. Genetically modified E Coli strains can synthesize extracellular curli nanofibers, which is an amyloid fibrous structural components present in biofilms. We have designed and assembled DNA constructs to produce curli fibers with the ability to reduce gold nanoparticles and a polydopamine-binding fusion protein. Two E. coli strains were transformed with the constructs to produce the melanin coated well-organized gold nanoparticles. Curli fibers were assembled with alternating structural curli protein, CsgA (repeat unit) segments and one of the CsgA units was conjugated to spy tag protein, while the other was conjugated to the peptide fragment (FlgA3) which reduces gold nanoparticles from the auric chloride solution. A fusion protein comprised of the spycatcher protein conjugated to the repeat unit of the Pnol17 amyloid fiber was created and the fusion lead to the formation of the gold nanoparticle-polydopamine conjugate. The goal of this study is to design and produce novel polydopamine-bound gold nanoparticles using synthetic biology approaches, to generate a preliminary model for future investigation of the feasibility and advantages of bacterially-produced tunable biocomposite materials, which could find applications in plasmonics and catalysis.

**SM03.02.01**

**Synthetic Biology for the Synthesis of Silicon-Containing Materials**

Maria J. Sanford1, 2, Chia Hung1, Maneesh Gupta1, Patrick B. Dennis3 and Matthew B. Dickerson4; Materials and Manufacturing Directorate, Air Force Research Laboratory; WPAFB, Ohio, United States; UES, Inc., Dayton, Ohio, United States.

Synthetic biology has garnered interest as a tool for the production of synthetically challenging materials. Recently, a facile bio-catalytic route to the synthesis of molecules containing carbon-silicon bonds has been reported, potentially connecting synthetic biology with the production of silicon-based materials. In this work, we report on our recent efforts towards the creation of a synthetic biology system to generate a wide range of novel, silicon containing polymers to be used as precursors for the production of robust, high-temperature materials. Ultimately, our goals are to leverage synthetic biology to create silicon containing precursor materials in an environmentally friendly, scalable manner, and to take advantage of the remarkable ability of biomolecules to self-assemble at multiple length scales to enhance the functional capabilities of the resulting high-temperature materials.

**SM03.02.02**

**Designing Diatoms—Characterization of Frustule Composition and Associated Optical Properties**

Sasha Teymorian, Joseph Labukas, James Snyder and Joshua Orlicki; U.S. Army Research Laboratory, Aberdeen Proving Gro, Maryland, United States.

Diatoms are microalgae that are particularly relevant for engineered living materials because they utilize silicon to create mineralized structures that are far more intricate and exhibit better mechanical properties than any synthetic counterpart. In this study, we seek to (1) harness the natural diversity of diatoms and (2) establish genetic control over silica morphogenesis to understand their unparalleled level of sophistication over nanotechnology. Herein, we compare the frustule composition of native strains under a variety of growth conditions, and discuss in detail implementation for strain optimization. In addition, we establish baseline optical properties and identify strains for potential applications in coatings, photonic materials and sensors. Taken together, our approach expands the understanding of accessible frustule morphologies through growth and genetic engineering.

**SM03.02.03**

**Synthetic Biology Challenges for Army Materials Applications**

Joshua A. Orlicki, James Snyder and Sasha Teymorian; Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

The emerging field of synthetic biology provides opportunity and new capabilities for the precision synthesis, assembly, and function of architectured materials. Currently, there are significant challenges for the integration of bio-derived and bio-based technologies in the defense-oriented materials space, in which materials are expected to perform under broad operating conditions. Army platforms must reliably operate over wide temperature ranges (e.g. -40 to 75 C) and extremes in humidity. In addition, materials must exhibit the durability to be fielded for long periods of time (e.g. 5+ years) and endure strain rate deformations from low strain, high frequency vibration to high strain impact events. We anticipate a significant challenge in harnessing synthetic biology to develop materials that are effective across this environmental breadth, particularly when considering that automated/parallelized biological experiments are not aligned to traditional materials science characterization strategies that typically occur in series and require much larger scale of material. This submission will give an overview of current projects employing the tools of Synthetic Biology and highlight needs of materials in context of the Materials & Manufacturing Science Division of the Army Research Laboratory.

**SM03.02.04**

**Halogenases for Chemical Production**

Rebecca M. Raig1, 2, Drew Wagner1, 2, Wendy Goodson1 and Maneesh Gupta1; Wright-Patterson Air Force Base, Air Force Research Laboratory, Dayton, Ohio, United States; Biological and Nanoscale Technologies, UES, Inc., Dayton, Ohio, United States.

Nature has acquired a vast repertoire of catalytic functionality. As the diversity of this repertoire is perpetually expanded upon by evolution’s process of random mutation and selection, a similar method may be employed to reprogram existing enzymes for novel function. Enzymes and their engineered variants have relevance where current production routes are lacking; they have the ability to improve product yield, materials price, supply chain security and/or environmental waste accumulation. This work aims to develop platforms for generating enzyme variants in order to facilitate production of molecules with desirable economic and industrial properties. As a starting point, we are investigating the screening and selection of halogenating enzymes for use in materials production. Several classes of halogenase are being examined for the ability to install chlorine, bromine, and fluorine into carbon frameworks. Our presented work highlights a single class of enzyme, the vanadium-dependent haloperoxidase, which displays a broad substrate reactivity...
profile, stability in organic solvent, and ease of recombinant expression and purification. In addition to performing bromination and chlorination, these haloperoxidases have also been shown to perform other potentially useful reactions such as hydroxylation, sulfoxidation, and epoxidation. We hope to eventually explore the manipulation of this enzyme and its reaction conditions to direct it towards the catalysis of specific substrates and chemical transformations.

SM03.02.05 Phloroglucinol Tri-Service Effort
Vanara Varaljay, Ali Saem, Steven Blum, Carrie Drake, Chia Hung, Adam Meyer, Rebecca Mickol, Nathan Schwalm, Drew Wagner, Adam Silverman, Theresah Zu, Wendy Goodson, Katherine Germaine, Sarah Glaven, Ben Gordon, Maneesh Gupta, Michael Jewett, Julian Lucks, Matthew Lux, and Christopher Voigt;
U.S., Inc., Dayton, Ohio, United States; MIT+ Broad Institute, Cambridge, Massachusetts, United States; US Army RDECOM, Baltimore, Maryland, United States; Air Force Research Laboratory, WPAFB, Ohio, United States; American Society for Engineering Education, Washington, District of Columbia, United States; RDRL SEE-B, US Army Research Laboratory, Adelphi, Maryland, United States; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; Northwestern University, Evanston, Illinois, United States; US Navy Research Laboratory, Washington, District of Columbia, United States; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; Ginkgo Bioworks, Inc., Boston, Massachusetts, United States.

Phloroglucinol (PG) is a precursor to TATB which is an energetic chemical of interest to the DoD. PG is part of the ‘Pressure Test’ as selected by DoD stakeholders for the MIT-Broad Foundry and is a compelling test case for the Tri-Service Synthetic Biology for Military Environment (SBME) research efforts. The Tri-Service Laboratories approached the PG single ‘challenge problem’ through leveraging SBME capabilities such as strain engineering capabilities, strain banks, and rapid prototyping of paper-based sensors. The AFRL team has an aircraft and a fuel isolate library enriched for “Promonomids,” which are known to harbor PG synthesizing enzymes known as PhD. The AFRL team has designed selective PhD primers for screening Pseudomonads isolates for diverse and potentially more active PhD enzymes than found in current literature. The NRL team is taking advantage of Marinobacter CP1’s (SBME chassis) ability to accumulate significant amounts of the PG precursor malonyl-CoA. Marinobacter will be genetically engineered to produce PG through a combination of genome editing to divert carbon to malonyl-CoA and the subsequent conversion to PG through the addition of a plastid-expressed PhD. The ARL team is harnessing the robust SBME chassis Clostridium acetobutylicum to model and optimize its capability to produce significant amounts of the PG precursor malonyl-CoA with plastid-expressed PhD. ARL has determined that mixed sugar inputs yield optimal PG production. Additionally, ARL will construct a living PG sensor in soil microorganisms using ICE technology obtained from the Voigt laboratory. The ECBC team and Northwestern University collaborators have developed and optimized a paper-based, cell-free PG sensor. The paper-based PG detection system will be used in field-deployable conditions where the sensor would be triggered by PG, resulting in rapid reporting of the presence of PG. The MIT-Broad Foundry has optimized PG production in the model chassis E. coli and has built a PG genetic sensor for rapid screening. The PG Tri-Service collaborative efforts in biological and cell-free systems will result in optimized PG production and detection, invaluable for DoD and synthetic biology applications.

SM03.02.06 Protein-Based Microcapsules as Alternative Way for Ruggedization of Functional RNA-Based Sensors
Nancy Kelley-Loughnane, Irina Drachuk, Svetlana Harbaugh, and Jorge Chavez;
Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson Air Force Base, Ohio, United States; UES, Inc., Dayton, Ohio, United States; Air Force Research Laboratory, 711 Human Performance Wing, Wright Patterson Air Force Base, Ohio, United States.

Conventionally, in vitro protein synthesis has been focused on a top-down approach when effective transcription/translation process relied on compartmentalization of the whole cell-free system in liposomal vesicles. In this method, having an appropriate phospholipid membrane fluidity played important role not only in the progression of protein expression, but also in mechanical stability of a very rigid osmotic system. Alternatively, protein-based vesicles prepared using bottom-up approach can solve some of the hurdles associated with liposomal vesicles. Assembled in a layered fashion, microcapsules afford tailored membrane porosity, variable DNA loading capacity and improved mechanical and chemical stability necessary for a prolonged shelf storage of RNA-based aptamers. We demonstrated that during layer-by-layer assembly, several DNA templates encoding various RNA-based aptamers and riboswitches can be immobilized in microcapsules prepared from reconstituted silk fibroin protein. Upon activation of RNA aptamers with a specific analyte, DNA templates immobilized in microcapsules were proven to be functional on transcriptional and translational levels. During incubation in a cell-free system, the rate of expression of a reporter gene was similar to the rate of expression for microcapsule-bound DNA templates, confirming that the functionality of aptamers was conserved. By increasing the loading capacity of DNA templates in microcapsules, the level of gene expression can be amplified. Further functionalization of silk shells with gold nanoparticles and antibodies will allow to expand multi-component DNA microcapsule complex design for targeted surveillance of several biomarkers. The proposed design of multifunctional protein-based microcapsules provide necessary robustness to RNA-based aptamers for their long-term storage or prolonged circulation, as microcapsule-bound DNA templates have been proven to be functional after one year storage at ambient conditions.

This research is funded by the Air Force Office of Scientific Research (AFOSR).

SM03.02.07 Gold Nanoparticle Assembled Gene Networks
Rajesh Nair, Patrick B. Dennis, Sanaz Farajollahi, Samantha Knoth, and Kathlyne Montgomery;
Air Force Research Laboratory, Dayton, Ohio, United States.

Plasmonic metal nanoparticles have interesting physiochemical properties that have been used for many applications including biosensors, cellular imaging and drug delivery. Conjugation between gold nanoparticles (AuNP) and biomolecules, proteins and nucleic acids expand these applications. Here, we applied the Polymerase Chain Reaction (PCR) to build a genetic circuit based on an oligo-conjugated AuNP foundation. Constructed gene networks are created using amplicons containing a T7 promoter followed by an open reading frame for a gene of interest and a T7 terminator. Our current focus is on optimizing PCR reaction for creating gold-conjugated gene networks as well as characterization of the AuNP-DNA complexes by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). With this approach, we plan to expand potential applications for the constructed gene networks by coupling the networks to cell free protein expression systems and exploring plasmic tunability of gene expression.

SM03.02.08 Hydrogel Encapsulated E. coli for Responsive Biomaterials
Drew Wagner, Cason Willey, Vincent Chen, Nathan Ferguson, Cheri Hampton, Chia Hung, Larry F. Drummy, Patrick B. Dennis, Wendy Goodson, Abigail Juhl, and Maneesh Gupta;
Air Force Research Laboratory, Beavercreek, Ohio, United States; UES, Inc., Dayton, Ohio, United States.

Microbial gas vesicles (GVs) are gas-filled protein microstructures encoded by biosynthetic pathways endogenous to marine bacteria and extremophiles and function to provide a way to control buoyancy by the host organism. Composed of a single layer of protein, gas vesicles are remarkable in that they exclude water from their interior despite forming in an aqueous environment. To explore materials applications of gas vesicles, we have transported a 10 gene GV operon onto an inducible expression vector and recapitulated vesicle assembly in E. coli cells. E. coli cells producing gas vesicles are further incorporated into hydrogels to create materials with tunable density that can be used to make environmentally-responsive biomaterials with variable acoustic properties. Further, we envision and are working towards altering the genetic control of the system to make GV-expression responsive to additional inducer signals and subsequently bio-print GV-expressing cells into gel-matrices to enable spatio-temporal manipulation of hydrogel properties.

SM03.02.09 Will Synthetic Acorns Grow into Biobuildings—Comparing the Coding Complexity of Natural Materials with the Software of Man-Made Systems
Joseph Riolo and Andrew J. Steckl;
University of Cincinnati, Cincinnati, Ohio, United States.

While the field of biology seeks to understand the functions and mechanisms of natural organisms, synthetic biology aims to use biological functions to engineer materials and systems. This engineering view is at the core of synthetic biology and seeks to define fundamental building blocks in nature that can be manipulated in a variety of combinations to design and produce complex systems. To illustrate this approach Ball compared the components and the level of complexity that goes into the design and manufacturing of an automobile to the process of biological cell formation – building materials (glass, metal vs nucleotides, amino acids); components (pistons, wheels vs proteins); modules (microcontroller vs genetic circuits), etc.

Barnatt asked a thought provoking question related to synthetic biology: “will synthetic acorns grow into biobuildings?” There are many aspects that need to be considered to begin to answer the question: 1. what materials that are needed for this quest; 2. what is the level of complexity involved; 3. what are associated building costs, are they
competitive. While this rhetorical question draws attention to the possibilities of synthetic biology, a rapidly growing community is exploring nearer-term applications (synthetic biochemical production, biocomputing, biosensors, etc.).

To partially answer this question we have initiated a study to characterize the complexity required to create engineered organic systems. While complexity is a relative term, computer software development can be a suitable benchmark due to similarities between instruction storing function of DNA and binary code. Further similarities between organic and software systems are the use of limited serial instruction sets (quaternary or binary) to produce arbitrarily complex outcomes when executed on deterministic systems.

The starting point is the comparison of the genome of different organisms to landmark software programming projects. The number of base pairs in the genome of organisms ranges from ~ 10 to 10 million for bacteria to ~ 1 billion for birds to a few billions for humans and other mammals. Major software projects for which some details (number of lines of code) are available have been selected for comparison, including the Hubble Space Telescope, the Mars Curiosity Rover, the Android smartphone operating system. The extent of compiled object code ranges from several hundred million to a few billion characters. The similarity between numbers of software characters in complex computer programs and base pairs in genomes, suggests that programming complex synthetic biosystems, while quite challenging and requiring a major effort, is likely to be feasible.

Biological coding provides additional functionality beyond storing of genetic information. Molecular structure and shape provide the means for reproduction of the genetic code, its transformation into amino acids and proteins, etc. This represents the storage of additional (2nd, 3rd order) valuable information that needs to be accounted in future analysis. It is important to note that genome size does not necessarily correlate with organism complexity. Interestingly, a similar case may be made for software programs, in that their size is not only related to the complexity of the system function but also on the computer language used, the period when the programming was carried out, other needs of the system, etc. Nonetheless, our preliminary evaluation indicates that the level of complexity involved in the genome of even the most sophisticated organism is comparable to large-scale man-made computer programs.


Cell-free protein synthesis (CFPS) is a promising approach for the production of biomaterials that cannot be synthesized by existing organic chemistry techniques. CFPS avoids many of the pitfalls of bacterial expression of biomaterials by allowing direct access to the chemical reaction that is taking place. Among the advantages of CFPS are increased tolerance to toxic reagents and products, facile incorporation of non-biological components such as abiotic amino-acids, the absence of cell transfection or protein purification steps, and increased yield as the CFPS system only makes the proteins it has been templated to produce. NMR monitoring of CFPS would allow us to fine-tune these systems so that they may be successfully scaled in a cost-effective manner. CFPS systems are commonly optimized via the production of green-fluorescent protein (GFP) which is spectroscopically monitored as the reaction proceeds. This approach fails in anaerobic environments since GFP chromophore maturation is oxygen dependent. Further, GFP fusions are not applicable for the production of small molecules. By utilizing radioisotope labeled substrates and various 1D and 2D techniques we expect to be able to monitor the utilization of substrates, generation of the desired products, and flux of related metabolites of various CFPS reactions. Significant differences in CFPS yield have been observed when reactions are prepared by different users and/or different cell lysates. NMR spectroscopy may be able to elucidate the mechanism behind this reaction variability. We have been able to identify metabolic differences between lysates prepared by different users. When the reactants and cell lysate used in CFPS are controlled, NMR metabolite profiles differ between users. The production of side products, such as ethanol and lactic acid, varies by user and by lysate utilized. In-situ NMR may be able to identify mechanisms for low product yield, discover undesirable metabolism pathways that are being activated, or if energy deficits are occurring.

8:30 AM *SM03.03.01  
**Synthetic Biology of Halomonas for Next Generation Industrial Biotechnology** George Guo-Qiang Chen; School of Life Sciences, Tsinghua University, Beijing, China.

Industrial biotechnology cannot compete with the petrochemical industries as it suffers from high consumptions on energy and freshwater, discontinuous processing, low product concentration and thus low product recovery cost as well as low substrate to product conversion efficiency. Therefore, to make industrial biotechnology competitive, we need develop Next Generation Industrial Biotechnology which is energy and freshwater saving and run in a continuous way instead of a batch way. Seawater based fermentation technology has been developed based on Halomonas halophaga in which is a chassis grown faster than E. coli. We have been able to assemble several multiple genes containing pathways in H. halophaga in production of various biopolymer molecules, chemicals and proteins. The growth patterns of the Halomonas spp. have been changed to influence the shapes of Halomonas spp. from short rods to long fibers, even further to large spheres, allowing more PHA accumulation and easy product recovery. The technology has been pilot tested in industrial setting (5000 L), it has been proven to be able to reduce PHA production cost at least 100%. The seawater technology should be able to improve the economic competitiveness of industrial biotechnology. We expect the technology can play an increasingly important role in the fermentation industries.

9:00 AM SM03.03.02  
**Photocatalytic Oxidation in Metal-Organic Frameworks Using E. coli Synthesized Porphyrins Ligands** Jared B. DeCoste, Marilyn Lee, Sergio Garibay and Ann Ploskonka; US Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland, United States.

Utilization of various photosensitizers in metal-organic frameworks (MOFs) for photocatalytic oxidation of toxic compounds has been of recent interest. Typically these MOFs incorporate pyrene, porphyrins, or organometallic photosensitizers into the organic linker of the MOF. However, through the utilization of solvent assisted ligand incorporation (SALI), a wide variety of compounds can be post-synthetically incorporated into the 3 nm pores of NU-1000. We report here the incorporation of protoporphyrin IX produced in E. coli via the Shemin pathway into NU-1000. Various porphyrins can be produced via the Shemin pathway including coproporphyrin and uroporphyrin. Each of these porphyrins have carboxylic acid handles that can be incorporated into NU-1000 via SALI. The inclusion of these porphyrins into NU-1000 improved the rate of photocatalytic degradation of the MOF toward the chemical warfare agent simulant for sulfur mustard, 2-chloroethyl ethyl sulfide. Utilization of synthetic biology in MOF synthesis opens up new pathways that are yet to be realized through the production of novel or difficult to synthesize ligands.

9:15 AM *SM03.03.03  
**Living Architecture—Synthetic Biology for Structural Building Materials** Wil V. Srubar III; University of Colorado Boulder, Boulder, Colorado, United States.

Imagine a world where the buildings in which we live, work, and play — the walls, the roofs, the floors, the windows — are grown, maintained, and healed autonomously by living microbial communities. Imagine architects of the future that swap their sketchbooks for genetic tools that encode the architecture of a building right into the DNA of those communities. Living architecture may soon be more than a vision penned in a science fiction novel. In fact, we are closer to realizing that vision than you think, thanks to interdisciplinary teams of researchers armed with a commitment — and the synthetic biology toolkits — to make that vision a reality.
Recent advances in metabolic engineering have enabled autonomous, high-fidelity biom manufacturing of useful chemical, mineral, and polymer building blocks that can be leveraged in the design and fabrication of construction materials and living architectures at the human scale. This presentation will highlight the research efforts of a highly interdisciplinary and collaborative team at the University of Colorado Boulder that is integrating synthetic biology, microbiology, materials science, and structural engineering to design and fabricate useful minerals (e.g., aggregates for concrete production) and polymers (e.g., styrene) for materials with commercial applications to building design and construction. In one study, we demonstrate the first time that calcium carbonate (CaCO₃) mineral aggregates for mortar and concrete can be tailored by modulating the precipitation kinetics through genetic engineering of ureolytic microorganisms. We also demonstrate that useful quantities of styrene for construction material manufacture can be biologically produced via microbial engineering. In this presentation, we will also show that engineered microorganisms can be leveraged in the design of hybrid living building materials that display both biological (i.e., living, regenerative self-healing) and structural (i.e., load-bearing) function. Finally, this talk will highlight the challenges that emerge working across length scales and disciplines, as well as the grand opportunity that exists for synthetic biologists and materials engineers to work together to create never-before-imagined material solutions for critical societal problems in energy, water, and the built environment.

9:45 AM SM03.03.04
Elucidation the Mechanism of Synthetic Riboswitches by Using Cell-Free Expression Systems Nancy Kelley-Loughnane1, Svetlana Harbaugh2, Yaroslav Chushak1,2 and Jorge Chavez2; 1Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson Air Force Base, Ohio, United States; 2Air Force Research Laboratory, 711 Human Performance Wing, Wright Patterson Air Force Base, Ohio, United States.

Biological systems have adapted diverse ways to control gene expression. Riboswitches are regulatory elements located in the 5′-untranslated region of mRNA that change the folded structure of the mRNA upon the binding of effector molecule and, as a consequence, alter the expression of the downstream gene. Besides the naturally evolved riboswitches that are triggered by cellular metabolites, several synthetic riboswitches have been developed that can sense and respond to non-endogenous small molecules such as theophylline, tetracycline or 2,4,6-trinitrotoluene (TNT). Majority of the synthetic riboswitches were selected and tested in the cell-based systems, usually E. coli. Cell-free protein expression systems (CFES) have several advantages for the development and testing of synthetic riboswitches including the elimination of the interaction with complex cellular networks and decoupling of transcription and translation processes. We studied the performance of theophylline-based synthetic riboswitch coupled with the sfGFP reporter gene in E.coli cellular extract and PURE cell-free systems. To monitor the mRNA dynamics a malachite green aptamer sequence was added to the 3′-untranslated region of sfGFP. Performance of the theophylline riboswitch was compared with a constitutively expressed sfGFP (control). Transcription dynamics of mRNA with riboswitch was very similar to the transcription of the control mRNA for all theophylline concentrations tested in both E. coli extract and PURE CFES. However, sfGFP expression in riboswitch construct was order of magnitude lower even at highest concentration of theophylline. This indicate that riboswitch altered the accessibility of the ribosome binding site and translation initiation rate. Dose-response curves showed similar behavior in both CFES with high micromolar to low millimolar dynamic range. The experimental effort was accompanied by computational modeling and simulations. A kinetic model of riboswitch activation was developed.

This research is funded by the Air Force Office of Scientific Research (AFOSR).

10:00 AM BREAK

10:30 AM SM03.03.05
Innovations in Performance Materials Enabled by Biology Adam Safir; Zymergen, Emeryville, California, United States.

As the desire for the latest product innovations continues, the need for new materials innovation has becoming a reality. New materials development would be made easier by having access to a new palette of chemical building-blocks, and such a palette of molecules with diverse structure and functionality is already available in nature today. Through the intersection of bioengineering, synthetic chemistry and material science, we at Zymergen are working to bring such novel building blocks to bear on materials innovation. In this presentation we will review our efforts in targeted rapid prototyping of biotarget production, and the development of diverse new materials useful in a variety of advanced product sectors.

11:00 AM SM03.03.06

Melanin is a pigment ubiquitous in nature and is found in all types of living organisms. Due to its unique physicochemical properties, high biocompatibility and biostability, there has been increasing interest in the use of melanin for biotechnological, biomedical and theranostic applications. In the vast majority of prior studies, melanin has been either chemically synthesized or isolated from animals, restricting its use to small-scale applications. In this study, we engineered the fast-growing marine bacterium Vibrio natriegens to synthesize melanin by expressing a heterologous tyrosinase gene. The V. natriegens melanin demonstrated characteristic electron paramagnetic resonance signals which were enhanced upon illumination. When melanized cells were immobilized at an electrode surface and probed with diffusible mediators and electrical inputs, we observed that melanization conferred redox activities to V. natriegens. The photoprotective properties of the bacterially-produced melanin were validated by its protection of bacterial and HeLa cells from UV irradiation. Moreover, melanized bacteria were able to quickly adsorb organic compounds such as chloroquine and trimethoprim. Providing the engineered V. natriegens strain with tyrosine or tyrosine-containing peptides as precursors led to the production of melanin nanoparticles and variants with varying optical properties, suggesting that this system is tunable and could be exploited for novel materials applications. Overall, the genetic tractability, rapid division time and ease of culture using comparatively inexpensive carbon sources provides a set of attractive properties that compare favorably to current Escherichia coli production strains and warrant the further development of this chassis as microbial factory for natural products synthesis.

Furthermore, we report results demonstrating the potential of Vibrio natriegens produced melanin in chemical protective scenarios. The fabric preparation utilized microwave initiation in the presence of (3-aminopropyl)triethoxysilane to provide primary amine groups on the surface. Analysis of water vapor transport through the melanin-modified fabric indicated that the treatment should have little impact on wearer comfort. The permeation of three chemical agent simulant vapors, 2-chloroethyl ethyl sulfide (CEES), methyl vinyl ketone, and 2,4-dinitrotoluene (DNT) was measured. The most dramatic outcome was 86% reduction in the peak rate and 90% reduction in the total amount of CEES vapor transported through melanin-treated fabrics compared to untreated control. These results suggest that the adsorptive properties of the inexpensive natural polymers can be further explored and tuned using standard synthetic biology tools to produce additional application relevant compounds. Ongoing work is considering differing melanin materials and their impact when considered in this application.

11:15 AM SM03.03.07
Bacterially-Produced Melanin as Biomaterials Chia Hung1, Annika Vaia1,2, Zheng Wang1, Gary J. Vora1, Wendy Goodson3 and Maneesh Gupta1; 1Air Force Research Laboratory, Wpafb, Ohio, United States; 2UES, Inc., Dayton, Ohio, United States; 3U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Melanin, a highly-coordinated polymeric nanoparticle found in natural pigments, has many intriguing properties including protecting organisms from ultra-violet radiation, ability to sequester reactive species and metal ions, and reported electrical conductivity. Melanin particles isolated from naturally pigmented sources are biologically templated with pre-defined shapes that dictate the optical and protective properties of the melanin assemblies. The tyrosinase enzyme is known to be involved in the biosynthesis of melanin, which lends credence to the use of a synthetic biology approach to engineer tyrosinase for melanin production. In this work, Bacillus megaterium tyrosinase was engineered and expressed recombinantly in Escherichia coli. Two forms of tyrosinase fusions were designed to be secreted through the curli export system and anchored on the cell surfaces. Using these systems, small melanin nanoparticles could be produced. In addition, melanin ghosts templated by E. coli cells were synthesized and characterized. Thus the tyrosinase expression, secretion and display capability that will be presented here represents a platform capable of allowing for the production colloidal melanin nanoparticles as well as melanin functionalized surfaces. Future work will investigate tuning the optical and electrical properties of the melanin assemblies through control of size and shape of the superstructure.

11:30 AM SM03.03.08
The Design and Creation of an Oxygen Sensing Protein Kinase Regulator for Synthetic Biology Applications Sanaz FarajiDjalali1, Patrick B. Dennis1, Ruth Pachter1, Andrew
The ultimate goal of this work is to design a novel cell signaling circuits that will trigger biochemical pathways in response to the oxygenation state of their environment. For this purpose, we use PAS domains which are sensing elements found in all living organisms that respond to environmental stimuli including, light, oxygen, redox state and various metabolites. To create new oxygen sensing genetic circuits, chimeras of the heme iron binding PAS domain from the prokaryotic B. japonicum histidine kinase (FixL) are being engineered with the ability to modulate the enzymatic activity of the mammalian PAS domain containing PAS Kinase (PASK), a protein kinase involved in the control of carbon metabolism and cellular energetics. Molecular simulations, coupled with ultrafast spectroscopic techniques, are being used to support the design and testing of the chimeras. Purified chimeras are also tested for their ability to inhibit PASK kinase activity at various oxygenation states, using a newly developed, non-radiological protein kinase assay. The function of these metazoan derived signaling elements will be probed in a prokaryotic system in order to generate orthogonal signaling pathways for cellular metabolic control.
need, use of indigenous or sustainable feed stocks, and leap-ahead advances in biobased materials and technology providing smart systems providing new protection and sensing capability in operationally challenging and contested environments. With increasing complexity and control the long-term vision is to develop advanced materials imparting living function for operation in Army relevant environments-disruptive capabilities, such as self-healing, adaptation, protection & situational awareness.

The continual convergence of synthetic biology with other fields and disciplines such as additive manufacturing, lab-on-a-chip, machine learning, and multi-scale computing promises to usher in a new age of manufacturing, leading to structural and multifunctional materials. Further, as our ability to control and sustain biological systems and understanding and control of self-assembly improves, we can begin to take these advances out of the laboratory to on-demand applications. To accomplish this, key components of our approach includes the development of advanced discovery to manufacturing pipelines, bringing both an understanding of structure-function relationships and ultimately rational design principles along with tools to unlock broad ranges of hosts for access to new material sets and sustainment in military environments. Bringing together materials and application experts across the physical and engineering sciences as well as government, academia and industry will significantly advance our ability to build discovery to product pipelines, with an emphasis up front on concept of operation, manufacturability, and logistics/sustainment.

This paper will present a discussion the challenges and opportunities that this burgeoning field and snapshot of the Army’s synthetic biology program including more detailed discussion of genetic control of the biological/materials science interface.

4:15 PM SM03.04.06
Resilient Living Materials Built Through Printing Bacterial Spores
Lina M. Gonzalez and Christopher Voigt; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

A route to advanced multifunctional materials is to embed them with living cells that can perform sensing, chemical production, energy scavenging, and actuation. A challenge in realizing this potential is that the conditions for keeping cells alive are not conducive to materials processing and require a continuous source of water and nutrients. Here, we present a 3D printer that can mix material and cell streams in a novel printhead and build 3D objects (up to 2.5 cm by 1 cm by 1 cm). Hydrogels are printed using 5% agarose, which has a melting temperature (65°C) consistent with thermophilic cells, a rigid storage modulus ($G' = 6.5 \times 10^5$ Pa), exhibits shear thinning, and can be rapidly hardened upon cooling to preserve structural features. Spores of R. subtilis PY79 are printed within the material and germinate on its exterior, including spontaneously in cracks and new surfaces exposed by tears. By introducing genetically engineered bacteria, the materials can sense chemicals (IPTG, aTc, xylose, or vanillic acid) and produce biopolymers (melanin).

Further, we show that the spores are resilient to extreme environmental stresses, including desiccation, solvents (ethanol), high osmolarity (1.5 mM NaCl), 365 nm UV light, X-rays, and g-radiation (2.6 kGy). The introduction of a metabolic pathway for melanin improves resistance to 254 nm UV light and g-radiation. The construction of 3D printed materials containing spores enables the living functions to be used for applications that require long-term storage, in-field functionality, or exposure to uncertain environmental stresses.

4:30 PM SM03.04.07
A Sea Worm Jaw Protein Promotes Heme Crystallization
Zachary Reiner1, 2, Andrea Poole1, 2, Maneesh Gupta2, Chia Hung2, Wendy Goodson1 and Rajesh Naik2; 1UES Inc., Beavercreek, Ohio, United States; 2Air Force Research Laboratory, Dayton, Ohio, United States.

Hemozoin, a crystalline form of heme generated by malaria-causing parasites, is an attractive alternative to other inorganic oxidizers for energetic materials due to a higher output when combined with nano aluminum (Slocik, J. et al. Small. 2015, 5538). Developing methods to control hemozoin crystal morphology should enhance current energetic capabilities. Histidine-rich proteins have been shown to promote hemozoin crystallization with sizes smaller than those obtained from synthetic methods. Here, we identify Nvjp1, a jaw protein from sea worm, as a capable catalyst of hemozoin formation. We also compare crystals nucleated from Nvjp1 to those of known hemozoin proteins when combined with nano aluminum (Slocik, J. et al. Small. 2015, 5538).

Ultimately, the ability to generate modular nanoenergetic materials will serve present and future military needs.

**SYMPOSIUM SM04**

Translational Materials in Medicine—Prosthetics, Sensors and Smart Scaffolds
April 23 - April 25, 2019

Symposium Organizers
Lucy Di Silvio, King's College London
Pankaj Gupta, Abbott
Deepak Kalaskar, University of Manchester
Sudipta Seal, University of Central Florida

* Invited Paper

SESSION SM04.01: Smart Materials/Scaffolds I

Session Chairs: Lucy Di Silvio and Sudipta Seal

Tuesday Morning, April 23, 2019

PCC North, 200 Level, Room 227 A

10:30 AM **SM04.01.01**

*In Situ* Tissue Engineering with a Surprisingly Smart Scaffold
Buddy Ratner; Department of Bioengineering and Department of Chemical Engineering, University of Washington, Washington, Washington, United States.

Tissue engineering has been with us for over 30 years and yet, I spite of some clinical successes, it has had little impact on the day-to-day practice of clinical medicine. This has been attributed to translational issues in scale-up and production, i.e., high costs; incompletely developed technologies and regulatory concerns. The concept of *in situ* tissue engineering is attractive in that it utilizes the patient’s own cells and also the patient’s own body as the bioreactor. Sphere templated porous polymers (*STPP*, where all interconnected pores are approximately 40 microns in diameter, have been found upon implantation to be rapidly infused with macrophages which then, in about 1 month, leads to vascularized, reconstructed tissue. Larger and smaller pore size materials do not demonstrate this phenomenon. Implantation of 40 micron pore STPP in bone sites yielded bone.

Implantation in sciera yielded sclera tissue. Implantation in skin showed reconstruction of both the dermis and epidermis. Implantation in heart led to reconstruction of the heart stroma. Recent investigation of this *in situ* tissue engineering reconstruction demonstrated that major changes are occurring in RNA signals from cells in 40 micron pores, compared to cells in 80 micron pores. Also, unique cells morphologies are seen in different pore sizes. Finally, there is evidence that the macrophages may be differentiating to an endothelial-like lineage contributing to the vigorous blood vessel ingrowth. (coauthors on this work are James Bryers, Neal Beeman and Le Zhou)

11:00 AM **SM04.01.02**

Silk—From Textiles to Medical Products
David L. Kaplan; Department of Biomedical Engineering, Tufts University, Medford, Massachusetts, United States.
Silk proteins have emerged from the textile and suture worlds into a broader suite of medical utility over the past few decades. This progression started with new fundamental insights into the features of this unique protein polymer, and has subsequently evolved into new utility for these polymers in terms of clinical impact. We will review the historical, research and translational steps that have supported new medical materials and devices based on silks. We will also speculate on the future directions for this protein polymer based on the progress to date and the medical needs of the future.

11:30 AM SM04.01.03
Supramolecular Hydrogels for Prevention of Post-Operative Adhesions
Eric A. Appel; Stanford University, Stanford, California, United States.

Post-operative adhesions represent an important, unmet clinical need with costs to the U.S. healthcare system exceeding $2.5 billion annually. Adhesions form as a result of normal wound-healing processes following any type of surgery and develop after 95% of cases. In cardiac surgery, adhesions are particularly problematic during redo operations where surgeons must release pericardial adhesions from the surface of the heart before the intended procedure can begin. This process significantly lengthens operation times and introduces significant risks of hemorrhage and injury to the heart and lungs during sternal reentry and cardiac dissection. This presentation will discuss the use of a dynamically crosslinked polymer-nanoparticle (PNP) hydrogel adhesion barrier comprising hydrophobically-modified biopolymers (BPs) and biodegradable PEG-PLA nanoparticles (NPs). We demonstrate these materials to have desirable linear viscoelastic, yield-stress, and flow properties permitting simple spray delivery, robust tissue adherence, local tissue retention over the course of weeks and complete resorption within one month, as well as robust prevention of pericardial adhesion formation. We show that it is the distinct mechanical properties of these materials that dictate efficacy. Overall, this presentation will demonstrate the utility of a supramolecular hydrogel system as an effective solution for the prevention of post-operative pericardial adhesions.

11:45 AM SM04.01.04
3D Human Eye Model Using Soft and Rigid Materials
Simon Regeil, Roger Delattre and Marc Ramuz; Ecole des Mines de Saint-Etienne, Gardanne, France.

We present here the development of a physical human eye model – based on hybrid soft/rigid materials - in order to create a test bench reproducing the optical eye properties. We have developed phantom eye tissues in order to mimick the different parts like the sclera or the ciliary body as finely as possible regarding the optical properties. As a matter of fact, these parts are crucial in order to mimic human eye but often neglected in the literature. For the development of these models, we used the optical parameters (absorption and scattering coefficients and refractive index) extracted from an experimental study carried out on porcine eyes – which are close to human one. Moreover, we present a soft actuated model of the iris where the aperture ranges from 1 mm to 8 mm. Finally, all the different parts are put together to obtain a device mimicking exactly the optical properties of an eye.
This model could use to test medical imaging like diffuse optical tomography.

SESSION SM04.02: Smart Materials/Scaffolds II
Session Chairs: Lucy Di Silvio and Sudipta Seal
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 227 A

1:30 PM *SM04.02.01
Designing 3D Smart Scaffolds for Biomedical Applications Exploiting Peptide Self-Assembly
Alberto Sainani; School of Materials and Manchester Institute of Biotechnology, University of Manchester, Manchester, United Kingdom.

The use of non-covalent self-assembly to construct materials has become a prominent strategy in biomaterials science offering practical routes for the construction of increasingly functional materials. A variety of molecular building blocks can be used for this purpose, one such block that has attracted considerable attention in the last 20 years is de-novo designed peptides. Peptides offer a number of advantages to the biomaterial scientists. The library of 20 natural amino acids offers the ability to play with the intrinsic properties of the peptide such as structure, hydrophobicity, charge and functionality allowing the design of materials with a wide range of properties. Synthetic peptides are chemically fully defined and easy to purify through standard processes. Being build form natural amino acids they result usually in low toxicity and low immune response when used in-vivo and can be degraded and metabolised by the body. The β-sheet motif is of particular increasing interest as short peptides can be designed to form β-sheet rich fibres that entangle and consequently form very stable hydrogels. Through the fundamental understanding of the self-assembly and gelation processes of these peptides across length scales [Gao J. et al. Biomacromolecules 2017, 18, 826] we have been able to design hydrogels with tailored properties for a range of applications from tissue engineering [D. Kumar et al. Adv. Funct. Mat. 2017, 27, 1702424] and cell culture [Castillo-Diaz L. et al. J. of Tissue Eng. 2016, 7, 2014173146649789] to drug delivery [Tang et al. Int J Pharm 2014, 465, 427], 3D bioprinting [Raphael, B. et al., Materials Letters 2017, 190, 103. and biosensing [King P. Et al. Chem. Comm. 2016, 52, 6697].

2:00 PM *SM04.02.02
Designing Smart Materials for Cell Modulation
Molly Stevens; Department of Materials and Department of Biengineering, Imperial College London, London, United Kingdom.

This talk will provide an overview of our recent developments in the design of smart materials for cell modulation. Bio-responsive nanomaterials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering (1) and recent examples in the design of nanostructured surfaces and elucidation of the cell-material interface will be presented [2, 3].


2:30 PM SM04.02.03
Smart Bone Mimetic Scaffolds as Cancer Testbeds
Kalpana Katti[1, 2, 3], MD Shahjahan Molla[1, 2, 3], Sumanta Kar[1, 2, 3] and Dinesh R. Katti[1, 2, 3]; 1Civil and Environmental Engineering, North Dakota State University, Fargo, North Dakota, United States; 2Center for Engineered Cancer Testbeds, North Dakota State University, Fargo, North Dakota, United States; 3Materials and Nanotechnology, Biomedical Engineering, North Dakota State University, Fargo, North Dakota, United States.

Regenerative medicine has led to many advances in tissue replacement therapies for hard and soft tissues. Besides the numerous coatings and putty-like products, tissue engineered manufactured constructs are also making headways for healing large defects. In addition, these tissue engineered constructs have a new application as testbeds for evaluating diseases. For instance breast and prostate cancer have the propensity to metastasize to bone at which point the disease is incurable. Lack of human samples at this stage of metastasis when patient is typically under hospice care and failure of animal models (since animals die before metastasis to bone) makes the humanoid test-bed a very advantageous dereve for studying cancer progression. We present a unique scaffold that uses biomimetic mineralization of hydroxyapatite inside nanocays galleries to make the hierarchical structure of human bone with a stoichiometric characteristic of new bone; a niche to which cancer cells migrate. Prostate and breast cancer cell lines are seeded on to this tissue engineered bone scaffold leading to the creation of tumoroids of cancer. We also demonstrate that this engineered test-bed duplicates the last stage of cancer metastasis as indicated by the gene expression and immunocytochemistry analysis of the tumors generated in the testbed. Metastatic and non metastatic cell lines of both prostate and breast cancer are evaluated at metastasis site indicating different and unique behaviours at bone site. Nanomechanical evaluation in conjunction with gene and protein expressions are done for cancer progression at bone site. We demonstrate that the nanomechanical evaluation can describe the progression of the disease. Thus, unique biomimetic smart scaffolds provide new opportunities to evaluate cancer metastasis.
Development of a Hybrid Hydroxyapatite-Baicalein Coating with Antibacterial Properties

Estelle Palierse1,2, Claude Jolivalt2 and Thibaud Coradin3; 1Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université, CNRS, Paris, France; 2Laboratoire de Réactivité de Surface, Sorbonne Université, CNRS, Paris, France.

More than 100,000 total hip replacements surgeries are performed each year in France1. Surgical site infections for these surgeries, mainly caused by the presence of microorganisms at the surface of the implant, are rare (0.5-5 % of the cases2) but can lead to serious damages such as implant failure and its removal. Currently, an efficient strategy for combating these infections is the use of systemic antibiotic prophylaxis. An alternative promising way to avoid its overuse is to use the implant as a support for the antimicrobial activity. Such a strategy allows the possibility of higher dosages near the affected site thereby improving efficiency and reducing the treatment duration and side effects3. Titanium alloy is widely used as material for body implant for its biocompatibility; nevertheless it cannot induce bone regeneration. In order to combine osseocoaudtion and local drug delivery, implants can be coated with a hydroxyapatite layer, the constituting mineral of bones, known to improve the osseointegration of implants4. The goal of this work was to develop an antibacterial coating on titanium alloy Ti6Al4V, associating a biomimetic hydroxyapatite and a natural antibacterial molecule, baicalein. This molecule is a flavonoid extracted from the root of the plant Scutellaria baicalensis, that has been used for a long time in the chinese traditional medicine for its antioxidants properties and of which the efficiency has been proved against multi resistant bacteria5. Hydroxyapatite coating was synthesized by immersion of the metal in a mineralizing solution called Simulated Body Fluid (SBF), whose ionic composition is similar to blood plasma, at physiological pH and temperature6. Hybrid materials were obtained either in a one-pot synthesis, with incorporation of baicalein in SBF, or in a two steps process consisting in the adsorption of baicalein at the surface of a pre-formed hydroxyapatite layer. Hybrid coatings were characterized by scanning electron microscopy, X-ray electron spectrometry, and both Raman and Fourier transformed infrared spectroscopies for their physico-chemical properties and for their antimicrobial activity. Finally, release of baicalein from both coatings was investigated, as well as their cytotoxicity and osteoinductivity. For purpose of comparison and understanding, a study of the molecular interaction between calcium and baicalein in solution was also performed.

References.
1 Haute Autorité de Santé. Prothèses de hanche. Phase contradictoire suite à la révision d'une catégorie de dispositifs médicaux. Saint-Denis La Plaine : HAS ; 2014.

SESSION SM04.03: 3D Printing
Session Chairs: Pankaj Gupta and Deepak Kalaskar
Tuesday Afternoon, April 23, 2019
PCC North, 200 Level, Room 227 A

3:30 PM *SM04.03.01
3D Printing of Biomaterials for Bone Disorder—Opportunities, Challenges and Clinical Significance
Susmita Bose; Herman and Brita Lindholm Endowed Chair Professor, School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington, United States.

Additive manufacturing (AM) or 3D printing (3DP) is becoming important for biomedical device fabrication, especially for patient matched implants due to lower cost and shorter lead time to manufacture. There are an estimated one million bone grafting procedures performed annually in the U.S. and a few million worldwide to repair bone defects, tumors, hip and knee replacements. Depending on the clinical need, different biomaterials are used for site specific or patient specific applications, for which different 3D printers are needed to create the biomedical device. Establishing process property relationships for different AM techniques are vital towards successful implementation of 3DP. However, additively manufactured components are still questioned for their reproducibility, machine to machine part quality variations and process specific material properties. Hard biomaterials, e.g., calcium phosphate (CaP) ceramics show significant promise towards bone implant applications, in both 3DP tissue engineering scaffolds and surface modified hip and knee replacement devices. We have used 3DP CaP scaffolds, for bone tissue engineering to control their degradation kinetics, mechanical strength, and biological properties with improved osteogenesis, angiogenesis and as drug delivery vehicle. An additional coating of polymer on both CaP scaffolds and hip / knee implant devices helped improve mechanical and biological properties while controlling the drug release kinetics. The presentation will include opportunities and challenges towards the use of 3DP or AM in developing biomedical devices.

4:00 PM SM04.03.02
Genomic DNA Functionalized 3D Printed Materials for Drug Capture
Daryl Yee1, Sankarganesh Krishnamoorthy2, Robert H. Grubbs2, Steven Hetts3 and Julia Greer1; 1Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States; 2Chemistry, California Institute of Technology, Pasadena, California, United States; 3Radiology, University of California, San Francisco, San Francisco, California, United States.

Since the discovery of chemotherapy in the beginning of the 20th century, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized due to the difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Working together with medical doctors, computational fluid dynamic experts, chemists, physicians and materials scientists, we report the fabrication of DNA functionalized 3D printed porous materials that can be used to trap doxorubicin, a commonly used DNA-targeting chemotherapy agent. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of attaching cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. The efficacy of these functionalized materials were demonstrated in PBS, where we observed a >70% reduction in doxorubicin concentration over a period of 10 minutes, highlighting the viability of this as a method of drug capture.

4:15 PM SM04.03.03
Advanced Digital Prosthetic Technology
Trevor Coward and Swati Jindal; Academic Centre of Reconstructive Science; Faculty of Dentistry, Oral & Craniofacial Sciences, King's College London, London, United Kingdom.

Digital technology has provided the maxillofacial and craniofacial team with the ability to manipulate digital images using various 3D software’s to provide additional information which can be applied to improving patient treatment outcomes. CT and MRI data can be used in conjunction with 3D printers to produce anatomical models of the skull and provide the surgeon with the advantage of planning the surgical procedure and preparing templates to act as guides during surgery to minimise tissue morbidity and reduce surgical time. Traditional methods of manufacturing maxillofacial prostheses are undertaken by hand carving the missing anatomical form in wax, and creating a mould into which pigmented silicone elastomer is placed. Over the last decade more modern technologies have been employed to manufacture anatomical face/body parts utilizing computed tomography (CT) data in conjunction with rapid prototyping (RP) techniques utilizing a hard plastic resin or thermoformed wax. However, these methods still require moulds into which a biocompatible pigmented silicone elastomer is placed.
The purpose of this presentation is to explore the development of direct printing of two component silicone elastomers in conjunction with a support structure to create complex shapes using a customized 3D printer. Ultimately, this would provide the maxillofacial prosthetist with a tool that manufactures prostheses reliably, with less emphasis placed on individual artistic interpretation. This technology has the potential to solve possible manufacturing solutions to complex shapes for both commercial and industry in addition to the current medical applications.

Method: The first step was to develop a two-component RTV silicone which was printable and had adequate properties suitable for fabrication of facial prostheses. The composition of silicone was varied to find the suitable combination with adequate strength. A 3D printer design had to be adapted to print the silicone.

Results: The base for two-component silicone was composed of 70% long, 20% medium, 10% short chain PDMS loaded with 30% filler showed optimal tear and tensile strength after printing. This newly developed two-component silicone also contained 5% cross-linker, 2.5% catalyst, 0.5% moderator and 3% thixotropic agent. The printer design and printing parameters were adapted to print the two-component silicone. Pigments were successfully printed through the printer and a hydrogel Pluronic F-127 was found to be suitable for printing colorful material for 3D printing of silicone prostheses.

Conclusions: The printing process and material have been developed to print silicone prostheses with suitable mechanical properties. The ways to incorporate colour data into printer and printing resolution need to research further.

4:30 PM SM04.03.04
Advances in Material Development and 3D Bioprinting
Hector Martinez; Cellink, Boston, Massachusetts, United States.

3D Bioprinting has gained attention in tissue engineering due to its ability to spatially control the placement of cells, biomaterials and biological molecules. The development of new hydrogel biomiks with good printability and bioactive properties has made it possible to 3D bioprint and accelerate the maturation of complex 3D tissue-like models. In this talk, we present our recent work in bioprinting and material development for 3D bioprinting and culture of healthy tissues such as skin, bone and cartilage, as well as cancer tissues for disease modelling and studies of tumor cells interaction with their microenvironment.

In addition to the biopink development we will be taking about printing thermoplastics, 4D-printing and soft robotics.

SESSION SM04.04: Poster Session: Translational Materials in Medicine—Prosthetics, Sensors and Smart Scaffolds
Session Chairs: Elizabeth Brisbois, Kalpana Katti and Sudipta Seal
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

SM04.04.01
Scaffold-Mimicked Silk/Gelatin-Based Neural Microelectrode Arrays Fabricated by Aqueous-Phase Microtransfer Printing
Zhen-Ting Tang and Wei-Chen Huang; Taipei Medical University, Graduate Institute of Biomedical Materials and Tissue Engineering, Taipei, Taiwan.

Traumatic peripheral nerve injury occurs prevalently in the worldwide, which usually results in the disability of extremities. Grafting with a nerve guidance artificial conduit to guide neuron regrowth can enhance nerve regeneration. However, the commonly used nerve conduit cannot provide a spatiotemporal regulation and in-situ monitoring for localized neurons. Accordingly, in this study, neural implant device that is combined with regenerative tissue scaffolds and microelectrode arrays was developed to enhance cell growth through applying electrical stimulation and neural signals recording in a as-built tissues-mimicked micro environment ent. A new type of tissues scaffold, called Dopa-SFG in the composition of synthesized doped-modified silk fibroin and gelatin was fabricated to exhibit tissue-mimic structural and mechanical properties, adhesive ability, and phase transition under a specific temperature. The aqueous Dopa-SFG precursors can be directly transformed to a gel bulk, in turn used to transfer print a complicated microelectrode structure that was pre-fabricated on PAA-C2- sacrificial layer. Such transfer printed scaffold-based neural microelectrode array enabled conformable adhesion on a moisture-rich curvilinear surface and electrical signals transduction from the tiny microelectrode site, which is expected to provide more efficient peripheral nerve regeneration.

Results and discussion: After cooling transfer, Dopa-Silk fibroin gelatin(Dopa-SFG) is bonded to the underlying MEA. In the liquid state, Dopa-SFG dissolves the sacrificial layer of calcium ions above the MEA, and then transfers the MEA to the hydrogel through the adhesion of Dopa. Thus, an adhesive silk protein sleeve electrode having electrical stimulation and contact-guided growth and monitoring functions is produced.

Reference:

SM04.04.02
Osteoinductive Thermoresponsive Conducting Hydrogels
Mayra C. Alcaraz and Jonathan Rivnay; Northwestern University, Evanston, Illinois, United States.

Regeneration of bone tissue in cases of non-union in fractures or spinal fusions present a significant medical and financial burden. Current approaches rely on scarce and undesirable allografts, new materials, or biologics, each presenting their own drawbacks and limiting efficacy. Electrical bone-growth stimulators have gained popularity with their promise of shorter recovery times; however, clinical meta analyses suggest mixed outcomes. Such invasive electrical approaches have relied on rigid wires inserted into the defect site. This approach is not ideal for regenerative engineering due to the remaining signaling and mechanical mismatch. To address this need, we turn to conducting polymers to develop a material that can fill the volume of a fracture defect site, allow for both passive and active stimulation of bone growth, and provide tissue-like characteristics. To this end, we demonstrate a thermoresponsive conducting hydrogel composite that shows differentiation of bone marrow stromal cells (BMSCs) into osteoblasts. The conductive hydrogel composite is based on a thermo-responsive hydrogel known as poly(polyethylene glycol citrate-co-N-isopropylacrylamide) (PCCN) sacrificial layer. Such transfer printed scaffold-based neural microelectrode array enabled conformable adhesion on a moisture-rich curvilinear surface and electrical signals transduction from the tiny microelectrode site, which is expected to provide more efficient peripheral nerve regeneration.

Results and discussion: After cooling transfer, Dopa-Silk fibroin gelatin(Dopa-SFG) is bonded to the underlying MEA. In the liquid state, Dopa-SFG dissolves the sacrificial layer of calcium ions above the MEA, and then transfers the MEA to the hydrogel through the adhesion of Dopa. Thus, an adhesive silk protein sleeve electrode having electrical stimulation and contact-guided growth and monitoring functions is produced.

Reference:

SM04.04.03
Direct 4D Printing via Polyurethane Paint Based Composites
Jheng-Wun Su1,2,3,4, Ezgi Tekin Pulatsu1,2,3,4, Jeng-Shin Liou1,2,3,4, Jia Wang1,2,3,4,5, Lin Ng1,2,3,4,5, Michael Lin1,2,3,4,5, Hsin-Yi Tsai1,2,3,4,5, Hsin-Tzu Huang1,2,3,4,5, and Hao-Pu Liou1,2,3,4,5

Direct 4D Printing via Polyurethane Paint Based Composites
Jheng-Wun Su1,2,3,4, Ezgi Tekin Pulatsu1,2,3,4, Jeng-Shin Liou1,2,3,4, Jia Wang1,2,3,4,5, Lin Ng1,2,3,4,5, Michael Lin1,2,3,4,5, Hsin-Yi Tsai1,2,3,4,5, Hsin-Tzu Huang1,2,3,4,5, and Hao-Pu Liou1,2,3,4,5

In recent studies, polyurethane has shown multiple properties that make it an excellent candidate material in 4D printing. In this study, we present a simple and inexpensive additive method to print waterborne polyurethane paint based composites by adding carboxymethyl cellulose (CMC) and silicon oxide (SiO2) nanoparticles to the paint. The first function of CMC and SiO2 is to improve rheological properties of the polyurethane paint for making a printable precursor, which improves the printing resolution and enhances additive manufacturability. Second, the composite precursors improve the curing rate of the polyurethane paint without changing its inherited shape memory properties. Third, the printed composite parts show enhanced mechanical strength compared with that of the parts printed with pure polyurethane. Finally, the 3D printed polyurethane-CMC and SiO2 parts exhibit time-resolved shape transformation upon heat stimulation. To the best of our knowledge, this is the first study of using the polyurethane paint as the precursor for
SM04.04.04 Optimizing Homogeneous Thin Solid Films (HTSFs) from µL-sized Blood Droplets via Hyper-Hydrophilic Coatings (HemaDrop™) for Accurate Constitutional Analysis via IBA, XRF and XPS

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Current blood diagnostics require 2-10 milliliters (mL) of blood per test, taking hours, or days, for results. Drawing mLs of blood can induce hospital-acquired anemia (HAA) in premature infants, and in chronically, or critically ill patients. Reducing the volume drawn while increasing analysis speed and accuracy can improve healthcare, and decrease suffering and costs from infections and transfusions. Rapid results from µL blood samples can revolutionize quality and cost of care.

Theranos claimed it could analyze nanoliter (nL) blood droplets. FDAs raids triggered by inaccuracies in tests, revealed Theranos diluted nL into mL-sized vials while using standard analysis methods with errors greater than the medically acceptable threshold of 10%. However, HemaDrop™, a “hyper-hydrophilic” surface coating, can solidify micro-liter (µL)-sized blood droplets within minutes microliter-sized droplets into Homogeneous Thin Solid Films (HTSFs), without phase separation or segregation. HTSFs can be analyzed within minutes using handheld or desktop analyzers, in air or in vacuo. Blood HTSFs were tested for accuracy in measuring electrolytes (Na, K, Mg, Ca, Cl) and hematocrit (Fe) from single µL droplets. So-called “Lytes & Crit” (electrolytes & hematocrit) are often the first tests conducted in ER, ICU, NICU, OR, and hospitals, as general status depends critically on hydration (electrolytes concentration), and oxygenation (Fe hematocrit levels). These are repeated daily and sometimes every few hours.

Repeated measurements show that electrolytes and Fe in human blood are accurate within 10% using IBA, XRF, and XPS, from a few µL of blood solidified as HTSF when calibrated using commercial Balanced Saline Solution (BSS+) pre-solidified on strips coated with HemaDrop™, called DropFilmStrip™.[1-3] XRF is of particular interest because it is a desktop/handheld tool which yields within minutes compositional analysis within the medically acceptable 10% for Na, K, Mg, Ca, Cl, Fe.

Prior to IBA, XPS, and XRF analysis, congealed, uniform HTSFs are compared to conventionally Dried Blood Spots (DBS). Solidification of droplets into HTSF is observed and timed via real-time microscopic and video. In DBS, phase separation between platelets and serum yields rough, non-uniform thin solid films. But HTSFs solidified on HemaDropTM are smooth, and uniform without phase separation. Similar behavior can be seen with solidified Balanced Saline Solution (BSS) droplets. BSS congealed on HemaDropTM exhibits little crystallization and no phase separation[4] while simply dried BSS does. HTSFs of human blood, canine blood and BSS solidified via HemaDropTM coated surfaces all underwent XRF in air, XPS in 10-10 Torr vacuo, and IBA in 10-7 Torr vacuo, performed on the same set of 5 and 10 µL-sized droplets congealed into HTSFs and compared to DBS. HTSFs yield identical, reproducible 2 MeV RBS, XPS, and XRF spectra on different areas of HTSFs. C, N, O, Na, K, Ca, Mg, Cl, Fe are detected with leading edges falling within IBA resolution (<15 keV, 2-3 channels), while DBS yield leading edges spread out over 100 keV.

The damage curve method extrapolates elemental composition while accounting for possible ion damage. Four consecutive spectra are taken on each analyzed area. RBS, XPS and XRF yields are interpolated to 0-analyzing down to extract concentration limits.

IBA simulations with the software SIMNRA are fitted to the RBS spectra and matched to within 1%. Atomic compositions from sequential IBA, XPS and XRF spectra taken on different areas of HTSFs yield different results. IBA, XPS and XRF results are within 5%.[5] Relative error analysis between multiple HTSFs establishes reproducibility within 10%. Comparative analysis from these results will be discussed to show how it guides optimization of the technology.


SM04.04.05 Supercritical Ti-Based Alloys Scaffold Prepared by Fiber Metallurgy Taehyun Nam; Materials Science and Engineering, Gyeongsang National University, Jinju, Korea (the Republic of).

Ti-50.3Ni-0.7Ag and Ti-18Zr-12.5Nb-2Sn (at.%) alloys scaffolds were fabricated by sintering the alloys fibers prepared by rapid solidification method. Secondary phases such as Ti₆Ni and Ti₆Ag phases which have been observed in the bulk alloy prepared by conventional casting method were not observed in as-solidified Ti-Ni-Ag fibers. Ag content in the fibers was measured to be 0.57% much larger than that in the bulk alloy, which is beneficial to improve the antibacterial function. The two stage B2-R-B19 transition occurred and good superelasticity with superelastic recovery ratio of 93% was observed in Ti-Ni-Ag fibers. As-spun Ti-Zr-Nb-Sn alloy fibers were composed of only the β phase. Tensile tests showed that Ti-Zr-Nb-Sn as-spun alloy fibers exhibited superelastic behavior over temperature ranges between 238 K and 318 K. A large recovery strain of 4.5% for 5% pre-strain was observed at room temperature.

In order to fabricate scaffolds, the fiber segments were put into the packing chamber of graphite mold and sintered at 1173 K for Ti-Ni-Ag alloy fibers and at 1573 K for Ti-Zr-Nb-Sn alloy fibers for 60 min in high vacuum condition. The alloy scaffolds prepared by sintering the fiber segments possessed three-dimensional and interconnected pores that were structured by the bonded small fiber segments with random directions. The porosity of the scaffolds were about 80%. The compressive strength of Ti-Ni-Ag alloy scaffold was about 5.6 MPa at the strain of 4% and that of Ti-Zr-Nb-Sn alloy scaffold was about 6 MPa at the strain of 7%, similar to that of cancellous bone ranging from 2 to 20 MPa. The elastic modulus of Ti-Ni-Ag and Ti-Zr-Nb-Sn alloy scaffolds was 0.67 GPa and 0.42 GPa, respectively, which were also similar to that of cancellous bone ranging from 0.1 to 2 GPa. Supercritical strain recovery of Ti-Ni-Ag and Ti-Zr-Nb-Sn alloy scaffolds was found to be 3% and 2.5%, respectively.

SM04.04.06 Controlled Rupture of Magnetic-Sensitive Microcapsules for Selective Fluorescence off-on Detection of Trivalent Cations Bowei Du, Yu-Ting Tai and Fu-Hsiang Ko; National Chiao Tung University, Hsin-chu, Taiwan.

Microcapsules are discussed in drug delivery, biomaterial and self-healing applications for their numerous advantages[1-3]. Plenty of stimuli are used to trigger the release of core contents[4]. However, any loss of core contents prior to their stimuli will lead to weakened function of encapsulated systems. In this research, materials of magnetic-sensitive microcapsules were successfully synthesized using Fe₂O₃/polycaprolactone (PCL) to construct the shell. In our previous work, pyrene based active Schiff base probe could be formed to complexes PE-M₃⁺ (M = Fe/Cr/Al) to detect Fe³⁺, Cr³⁺ and Al³⁺ ions by its nano-aggregation induced emission enhancement (AIEE)[5]. As we known that Fe³⁺, Cr³⁺ and Al³⁺ ions are essential in the human body, Cr³⁺ plays an important role in the maintenance of an effective carbohydrates, lipid and protein metabolisms[6-7]. In addition, Cr³⁺ ion has high biological activity while diabetics can cause Cr deficiency in the body. Hence, we designed a new probe that also can perform in a magnetic field though it moves through digestive tract. In order to protect the core content and control release of encapsulated cargo that utilize microcapsules-based drug release system and high-frequency magnetic field (HFMF) to accelerate the rate of contents release. A pyrene based Schiff base derivative 2-((pyrene-1-ylmethylene)amino)ethanol (PE) was encapsulated for sensing Fe³⁺, Cr³⁺ and Al³⁺ ions to use in the fluorescence turn-on responses. Furthermore, the solvent evaporation method was used to fabricate the microcapsules using W/O emulsion. Experimental observations showed that the magnetic nanoparticles in the shell structure indicated that the shell structure was subjected to a sharp structural change when the magnetic NPs caused rapid heating when exposure to a HFMF. After the magnetic particle PCL shell was degraded in the surrounding, in the same time, Schiff base probe PE was released into environmental solution also. In particular, the activity of the “OFF-ON” fluorescent sensor was not being obviously affected by encapsulated phenomenon. As shown in experimental observation, upon the increased addition of water fraction (fw) from 0% to 80% towards PE microcapsules in CH₂CN, the UV/PL peaks at 425/413 nm were red shifted to 463/470 nm, respectively.

This encapsulated fluorescent sensor exhibited a longer shelf life and better stability compared to the original sensor. The capsules’ shell improved the thermal stability of encapsulated PE, the thermal decomposition of these microcapsules around 350 deg. Likewise, the naked eye and fluorescence turn-on sensing responses were still performed well based on the Schiff base probes and PL spectra. The magnetic field and PE microcapsules showed an “instantaneous” burst release of drug by rapid temperature raise to induce a quick melting of the PE microcapsules. Therefore, the combination of magnetic and thermal properties would be a very attractive for detection of metal ions in organisms.

Keywords: Microcapsules; Magnetic-sensitive; Fe³⁺/Cr³⁺/Al³⁺ nanorobots; PCL; Fluorescent sensor; Trivalent cations; High-frequency magnetic field (HFMF)
Articular cartilage repair poses a great challenge to the medical community due to the avascular nature and poor intrinsic healing capacity. Bone marrow derived mesenchymal stem cell (BMSC) transplantation shows great promise to prevent subsequent damage to the injured area and to reconstruct cartilage. Nevertheless, the limited regenerative abilities of the BMSC, and low survival rate and incomplete differentiation in hinder further applications. Addressing these hurdles, researchers have designed several strategies, such as 3D cell spherical and bioscaffolds that mimic the natural tissue microenvironment to deliver physical and soluble cues. However, several pertinent impediments hinder advances in stem cell transplantation, including poor integration of cell-cell interaction and cell-ECM interaction into single system, and the diffusional limit of approximately 150-200 μm restricts the mass transportation of nutrients and growth factors.

To this end, we report a novel biodegradable MnO$_2$/gelatin nanomaterial to induce BMSC assembling and to control the chondrogenic differentiation of assembled BMSC in a highly selective and efficient way. Further, as a proof-of-concept demonstration, we utilized MnO$_2$-nanofiber as both cell-adhesion substrate and a chondrogenic inducer-delivery carrier with enhance stem cell differentiation in vitro and in vivo. Specifically, our novel nanoreinforced cell hydrogels have several advantages: (i) unique topographical properties to better mimic native cartilage microenvironment; (ii) integration of cell-cell interaction and cell-ECM interaction; (iii) highly efficient growth factor loading and spatiotemporal release capacity; (iv) highly stretchable and injectability; and (v) innovative magnetic resonance imaging (MRI) property. Our nanoreinforced cell assembling method shows great therapeutic potential for advanced stem cell transplantation and cartilage regeneration.

Effect of Photo-Initiators on Polymerisation of Thiol-ene Clickable Gelatin Bioinks

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Bioprinted scaffolds with physico-mechanical properties mimicking the native extracellular matrix (ECM) environment holds great potential for successful regenerative medical treatments and/or 3D models of cellular behaviors. Recent advances highlight alkylated gelatin (GelAGE) as a versatile hydrogel platform for both lithography-based and extrusion-based biofabrication with highly tailorable properties. This material is further known to be susceptible to photo-crosslinking with both UV- and Visible-light based photoinitiator systems. It is, however, unknown how these different photoinitiator systems affect long-term mechanical and rheological properties of GelAGE for the fabrication of tissue constructs with clinical relevant sized since UV light is known to be harmful for cells.

This study therefore aimed to study the polymerisation of GelAGE with UV (Irgacure 2959) and visible light (LAP, Ru/SPS) photoinitiators and concentrations suitable for lithography-based and extrusion-based printing applications based on resulting physico-mechanical and rheological properties. Gelatin was reacted with 12 mmol of allyl glycidyl ether (AGE) and 2 mmol NaOH per gram of gelatin at 65°C for 1h followed by dialysis, lyophilisation and NMR characterization. Hydrogel constructs were photo-polymerised (30mW/cm$^2$, 3min, 20wt.-% GelAGE) with linear dithiothreitol (DTT) at 1:1.5–1:6 AGE:SH molar ratios and different photoinitiators using either visible-light (450nm, 0.05wt% Lithium phenyl-2,4,6-trimethylbenzoylphosphinate; LAP or 0.2-1mM ruthenium; Ru and 2-10mM sodium persulfate) or UV-light (365nm, 0.05wt% Irgacure 2959) for 15min. Depth of cure, shape retention, viscosity, compressive modulus, mass loss, and mass swelling ratio were further characterized. Mechanical properties of photoinitiator systems was further studied as a function of time for hydrogels crosslinked with Ru/SPS and LAP. GelAGE was successfully synthesized (DodM:42) and fabricated through 10mm large constructs. Compared with Ru/SPS and Irgacure 2959, hydrogels with LAP demonstrated a higher degree of cure, shape-fidelity and homogenous polymerisation. Depth of cure was independent of DTT concentration (10.58-10.84mm), unlike hydrogels with Ru/SPS or Irgacure 2959. Better shape retention was also observed for LAP samples post swelling, the one with 1:1.5 AGE:SH molar ratio (partially dissolved, height drop to 6.32nm). GelAGE with UV photoinitiator (Irgacure 2959) resulted in lowest depth of cure and worst shape fidelity. The viscosity was observed to increase both with time of curing and dependent on the DTT concentration (0min = 10$^2$ Pa s, 15min = 3x10$^3$ Pa s for 1:1.5 AGE:SH molar ratio, 0min = 10$^2$ Pa s, 15min =1.7x10$^2$ Pa s for 1:6 AGE:SH molar ratio) which could be used to extend the fabrication window for extrusion-based bioprinting. The mechanical strength of Ru/SPS polymerised GelAGE constructs was further shown to be time-dependent (0min = 8.2 kPa, 10mm = 34 kPa, 30min = no hydrogel formation) and tailorable with different ratio of Ru:SPS and weight percent of GelAGE. Further replenish of SPS resulted in stiffer close to original value at t=0. Mass loss and swelling ratio were observed to be time-dependent as well. The time-dependent relationship of mechanical properties observed could be a powerful tool to achieve seamless mechanical gradients in biofabricated constructs by either bypassing processing for a short term or replenish SPS at certain time point.

In conclusion, GelAGE with LAP initiated polymerization offers a thiol-ene clickable biocompatible hydrogel platform that can be applied to fabricate clinical relevant sized tissue constructs with high fidelity and shape retention. In addition, the Ru/SPS system can provide a wide range of stiffness and gradient stiffness formation while the viscosity can be adjusted by varying DTT concentration to fit extrusion-based printing. All these results support the use of visible light photoinitiators but rather than UV photoinitiator.

Bioprinted 3D Hybrid Nasal Cartilage with Integrated Functional Olfaction

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Recent advances in microfabrication and biomaterials techniques have opened new doors to regenerate and recapitulate human organs in vitro with adequate levels of functionality required for regenerative medicine and drug development. Such advancements have enabled simultaneous targeting of the two challenges in nasal reconstruction surgeries: (i) high precision and personalized reconstruction of the nasal cartilage implants, (ii) retention of the olfactory epithelium and odor perception. The new hybrid nasal organ can be equipped with remarkable capabilities such as augmented odor detection and new levels of olfactory perception. Herein, we present precise reconstruction of the nasal cartilage using chondrocyte cell-laden photo-cross-linkable biomaterials as boneink and multi-material 3D bioprinting technique to fabricate a 3D cartilage tissue construct with tunable stiffness. In addition, by embedding vasculature in the macro-scale printed construct, we have also demonstrated the competence of our system in providing macro-scale viability and improved recapitulation of the cell behavior in 3D cartilage tissue construct. The engineered nasal cartilage tissue construct has been fully integrated with an electrochemical biosensing system to bring functional olfactory sensation. Functionalized with a variety of protein-ligand binding forms, including peptide-bacteria, antibody-virus, and peptide-chemicals, the developed nasal construct is capable of tunable selectivity towards specific airway disease biomarkers, explosives and toxins. With confirmed biocompatibility in integration with viable cartilage-like tissue, the proposed hybrid organ can lay the ground for creation of functional cellular biologic interfaces and humanoid cyborgs.
SM04.05.03
Design New Material Interface with Neurons for Neuron Stimulation and Regeneration

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Access and adoption of advanced prosthetics for children has been limited due to a variety of factors including: high costs, limited insurance coverage options, challenges in adaptation and training leading to high rejection rates, and limitations in technology or performance. These factors have driven prescribers to limit prescriptions of advanced prosthetics for children with congenital amputations, which occurs in approximately 5 out of 10,000 live births. Significant progress is needed to advance the field not only in the technology be developed, but also in the overarching training and feedback provided to the patients. In this study we discuss new techniques that have been integrated to advance the design in wearable neuroprosthetics, and a gamified, visual approach to training in the pediatric environment.

This work has demonstrated the effectiveness of using electromyographic (EMG) actuation in gamified simulations to train the actuation of multiple hand position gestures in a virtual environment. This type of training leverages real time visual feedback to user inputs, in this case muscle flexure with varied magnitude and time dependent patterns. This provides a stronger link between the intentionality capture (input) and the assigned thresholds and patterns required to activate the multiple states (outputs). This is implemented as a game that simulates the control of the prosthetic and translates the EMG input into functional game mechanics, providing meaningful feedback in form of gameplay. Initial studies have focused on testing the signal actuation repeatability to target specific multi-point magnitude set thresholds, and have shown promising results.

The role of additive manufacturing in medical devices has been developing both in practice and in the regulatory framework. The FDA’s new non-binding best practices have been key towards standardizing process flow and ensuring repeatable. The device developed in this study has been produced using 3D printed acrylonitrile butadiene styrene (ABS) plastic, via fused deposition modeling (FDM), including a dissolvable acrylic copolymer to allow for complex internal channels. Interlocking parts are created to interface with mechanical components including: fasteners, springs, and cabling. The advantages of this type of manufacturing allow for rapid prototyping, custom sizing for short run manufacturing, and the ability to grow modular parts that can be used to resize the antebrachial and brachial segments. These parts have demonstrated exceptional strength to weight ratios and durability. Print orientation, orienting the fiber deposition direction in context with the part and applied mechanical loads, is critical to achieving durability.

To achieve quantifiable outcomes, including arm system performance and the influence on patient’s quality of life, a clinical trial protocol for assessment has been developed in conjunction with Oregon Health & Science University (OHSU) and the University of Central Florida (UCF). This protocol includes assessment data points four times across the course of the one year study. Occupational therapists from OHSU will support the evaluation and provide valuable insight as to when multi-gesture hand states are appropriate to “unlock” for the patient. This novel development of technology and clinical translation is critical to advancing the accessibility of advances prosthetics for pediatrics. The use of additive manufacturing has enabled significantly lower costs, rapid prototyping, and advanced customization critical to improving clinical outcomes and experience.

9:30 AM SM04.05.04
Implantable devices and scaffolds with new functions interfacing with neural systems enables new techniques to fire and reconnect neurons. Specifically, we will report our recent progresses on a fiber based photoacoustic converters for successful in vitro and in vivo neuro stimulation and a biocompatible silk-based nanoladder scaffolds for facilitating neuron functional connection after injuries. In the first application, we design and develop a miniaturized fiber with diameters ranging between 500 microns to 1 millimeter composed of two layers: a diffusion layer and a expansion layer with nanocomposites to produce high intensity and controlled frequency of localized ultrasound when excited with nanosecond laser light. In vitro and in vivo neuron stimulation was successfully achieved with a laser duration of 20 milisecond. Neural stimulation in motor cortex of intact awake mouse brains confirmed the stimulation was localized with a high spatial resolution of 500 microns and not through direct auditory stimulation. In the second application, we design and demonstrate a silk-based scaffold composed of micron size fibers and nanoscale protrusions to direct axon growth along a predefined direction and facilitate neuron functional reconnection in vitro and in vivo.

Perineural invasion (PNI) is the neoplastic invasion of nerves. However, the mechanisms underlying its pathogenesis remain largely unknown. In this study, we created a hydrogel biochip to mimic a nerve tissue microenvironment for investigating the interaction between schwann cells and cancer cells. A new type of conductive tissue scaffold was developed via conjugating gelatin with poly(3,4-ethylenedioxythiophene (PEDOT), within which a naturally occurring polymer, melanin was incorporated to improve electrical properties. The resultant composite exhibited porous 3D structure with elastic conductivity and high chemical stability. The existence of Melanin and PEDOT was analyzed by FTIR confirming the bonding. Through SEM image we observed 300 nm spherical Melanin nanoparticles and PEDOT polymer both embedded in the hydrogel pore walls. The analysis of physicochemical characteristics indicated the electrical and mechanical properties increases as melanin and PEDOT incorporate with hydrogel. Furthermore, the in vitro biodegradation of compound showed a decreasing current as the conductive materials increases. At last we use the compound to create a hydrogel-based Electrode texture by transferprinting technique. As a result, a degradeable nerve-mimicking biochip was formed to investigate Perineural invasion.

9:45 AM SM04.05.04
Ultra compliant Gelatin-Based Conductive Microelectrodes Applied Fore Mimicking Neuro Microenvironment of Perineural Invasion

Yue-Xain Lin and Wei-Chen Huang; Taipei Medical University, Taipei City, Taiwan.

Implantable devices and scaffolds with new functions interfacing with neural systems enables new techniques to fire and reconnect neurons. Specifically, we will report our recent progresses on a fiber based photoacoustic converters for successful in vitro and in vivo neuro stimulation and a biocompatible silk-based nanoladder scaffolds for facilitating neuron functional connection after injuries. In the first application, we design and develop a miniaturized fiber with diameters ranging between 500 microns to 1 millimeter composed of two layers: a diffusion layer and a expansion layer with nanocomposites to produce high intensity and controlled frequency of localized ultrasound when excited with nanosecond laser light. In vitro and in vivo neuron stimulation was successfully achieved with a laser duration of 20 milisecond. Neural stimulation in motor cortex of intact awake mouse brains confirmed the stimulation was localized with a high spatial resolution of 500 microns and not through direct auditory stimulation. In the second application, we design and demonstrate a silk-based scaffold composed of micron size fibers and nanoscale protrusions to direct axon growth along a predefined direction and facilitate neuron functional reconnection in vitro and in vivo.

10:00 AM BREAK

10:30 AM **SM04.05.05
Two Photon Polymerization-Based Additive Manufacturing of Microstructured Medical Devices

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Laser-based additive manufacturing techniques such as two photon polymerization, matrix assisted pulsed laser evaporation-direct write, and laser induced forward transfer have been used over the past two decades to create surfaces with small-scale features for medical applications. For example, the two photon polymerization technique involves use of femtosecond laser (e.g., a titanium:sapphire laser) pulses for selective polymerization within highly localized regions of a photosensitive resin. Polymerization and hardening occur at sites within the photosensitive resin where the excitation threshold of the photoinitiator is exceeded. Polymerization of microscale and sub-microscale features is possible since the two photon absorption exhibits a nonlinear relationship with the incident light intensity. Two photon polymerization has been used to prepare structures with sub-microscale features out of photosensitive acrylate-based polymers, zirconium oxide hybrid materials, and organogelated ceramic materials. Several types of medically-relevant structures, such as scaffolds for tissue engineering and medical devices, have been prepared using two photon polymerization. For example, we have used two photon polymerization to prepare small-scale lancet-shaped devices known as microneedles for transdermal delivery of pharmacologic agents or transdermal sampling of body fluids. Efforts to optimize the two photon polymerization processing procedures and postprocessing procedures for medical applications will be considered. In addition, selection of an appropriate photoinitiator for use in medical applications will be considered. The biological and functional evaluation of two photon polymerization-created medical devices and scaffolds for tissue engineering will be described. Necessary steps in the development of two photon polymerization as a commercially viable manufacturing method will be described.

11:00 AM **SM04.05.06
3D Printable Bouncing Hybrids for Cartilage Regeneration

Julian Jones; Imperial College London, London, United Kingdom.

Orthopedic surgeons need devices that can replace the articular surface of cartilage, then regenerate the cartilage to replace the device, all while recruiting cells from the underlying bone marrow. Such devices do not yet available, but they could be, using our new hybrid biomaterials. Hybrids have nanoscale co-networks of inorganic glass and organic components, e.g. sol-gel silica and biodegradable polymers. We now have hybrids that can “bounce” and self-heal. The hybrids are ideal for 3-D printing inks, which can yield bespoke scaffold architectures. Osteochondral devices can now be 3D printed that stimulate articular cartilage production and also provide the bearing surface with tribology similar to native cartilage.
Bone implants are frequently used to treat osteoarthritis and reconstruct large bony defects. The aging population as well as increasing numbers of obese patients will enhance the future need for orthopedic implants. Although the use of these implants in total joint replacements has become one of the most successful procedures in medical practice, two major challenges remain: implant-associated infection and implant longevity. As a result, the bar for proper functioning implants has been raised: implants should ideally prevent infection by bacteria that are increasingly resistant to antibiotics as well as induce and support sustained tissue integration between implant and surrounding bone tissue to secure implant longevity. Both requirements can be fulfilled by bone implants with multifunctional surfaces that we have synthesized through a combination of rational design, selective laser melting (SLM) and plasma electrolytic oxidation (PEO) in the presence of metallic nanoparticles (NPs).

Additive manufacturing has boosted new research areas in which the functionalities of biomaterials do not depend on the material properties but are direct consequences of the topology and can therefore be rationally designed. This has enabled the synthesis of highly porous biomaterials that closely mimic the mechanical properties of native bone. Furthermore, geometrical features such as porosity, pore size and curvature can be rationally designed to promote tissue integration. However, porous biomaterials are at risk for infection as they may have surface areas up to several orders of magnitude larger than solid biomaterials. Therefore, it is essential to biofunctionalize the surface such that not only bone regeneration is improved yet simultaneously infection is prevented.

Here, we present the synthesis and characterization of multifunctional titanium bone implants. We designed long porous implants that were synthesized from medical grade Ti-6Al-4V powder by SLM resulting in porous implants with a 4 times enlarged surface area compared to solid implants. Subsequently, the implant surface was biofunctionalized by PEO using an electrolyte consisting of Ca/P species and Ag, Cu and/or Zn NPs. PEO is very suitable for highly porous structures as it generates a homogeneous oxide layer in which the NPs become entrapped, thereby preventing nanotoxicity. Following biofunctionalization, biomaterial surface morphology was analyzed by scanning electron microscopy, chemical analysis by energy dispersive X-ray spectroscopy, phase composition by X-ray diffraction and ion release kinetics by inductively coupled plasma optical emission spectroscopy. Antibacterial testing was performed against methicillin-resistant *Staphylococcus aureus* (MRSA), a pathogen commonly involved in implant-associated infection. We determined the antibacterial leaching activity in a Kirby-Bauer assay and quantified bactericidal activity in vitro as well as in an ex vivo murine infection model. Subsequently, through live/dead staining, metabolic assays and measurement of alkaline phosphatase activity the cytotoxicity and osteogenic differentiation of human mesenchymal stem cells (hMSC) were analyzed.

PEO biofunctionalization of the porous titanium implants resulted in a micro/nano-porous TiO$_2$ surface layer that contained hydroxyapatite. The immobilized NPs in the surface generated the release of Ag, Cu and/or Zn ions for at least 28 days resulting in strong antibacterial leaching activity and prevention of bacterial adhesion in vitro and ex vivo, with AgNPs demonstrating the largest antibacterial activity. The biofunctionalized surfaces did not induce cytotoxicity and improved the metabolic activity of hMSC. Altogether, the biofunctionalized porous titanium implants presented here are suitable candidates for further preclinical development to prevent implant-associated infection and improve implant longevity.
induced one particular cellular orientation as the fibroblasts followed and oriented along the capillary long-axis while the flat plate-like regions of the prosthesis, which initiates the foreign body response of the patient’s immune system leading to inflammatory bone loss. Bone loss may also be the result of stress shielding, caused by the mechanical mismatch of the bone-implant interface. With the introduction of a metallic implant, the physiological loading condition of the bone changes, since most of the load is carried by the implant. According to Wolff’s Law, this will cause bone to adapt itself by reducing its volume in places it is no longer needed. Biomaterial optimization is therefore inevitable, when working towards the next generation of life-lasting implants.

The emerging concept of metamaterials offers a promising route to the development of such implant biomaterials with unique combinations of mechanical (e.g. Negative Poisson’s Ratio (NPR)), mass-and fluid-transport (e.g. diffusivity and permeability) and biological properties (e.g. tissue regeneration performance). The topology of these so-called meta-biomaterials, may be rationally designed to exhibit unprecedented properties for tissue regeneration and sustained mechanical support. The tremendous developments in metal additive manufacturing have allowed us to fabricate these highly complex micro-architectures, including triply periodic minimal surfaces and hybrid combinations of auxetic and conventional meta-biomaterials.

Unlike conventional meta-biomaterials, auxetic meta-biomaterials have a negative Poisson’s ratio and expand laterally in response to axial stretch. A recent study has proven their importance within the field of orthopedics, where a rational distribution of negative (auxetic) and positive Poisson’s ratios was used to improve implant-bone contact and potentially implant longevity in the femoral component (i.e. hip stem) of a Total Hip Replacement (THR). Since the hip stem is repeatedly loaded under bending, the lateral side of a conventional implant will be retracting from the bone under tensile loading. The bone-implant interface is not only more susceptible to failure when subjected to tension, but the implant’s retraction also reduces bone-implant contact and allows wear particles to enter the bone-implant interface space. Laterally applying an auxetic meta-biomaterial therefore resulted in compression on both of the implant’s contact lines with the surrounding bone, decreasing the chance of bone-implant interface failure and stimulating osseointegration.

In this work, we characterize the mechanical properties of additively manufactured, titanium auxetic lattices, based on the re-entrant hexagonal honeycomb. The mechanical properties of auxetic meta-biomaterials are inherited from the auxetic property of Poisson’s ratio, which is got to be a value of 0.75 through slight hindrances. The limit micro-architecture of Laser Melting (SLM) process was explored to synthesize structures with optimal bone-ingrowth properties. Their architecture was therefore evaluated using micro-CT, while its quasistatic and fatigue properties were assessed in a compression test. The Poisson’s ratio was experimentally determined using Digital Image Correlation (DIC), based on the movement of a randomly applied speckle pattern. With this comprehensive library of mechanical and morphological properties, we hope to contribute to the adoption of auxetic lattices within the field of orthopedics, as an ideal substitute for bone in life-lasting implants.

We will report a throughput electrical biosensing system to rapid assess the human health and environmental toxicity of nanoscale materials to find the kinetics of nanotoxicity at cellular level. In this project, we developed a unique biosensing system for analyzing nanotoxicity assays of gold, silver, cadmium oxide and carbon nanotubes nanomaterials. An array formatted electrical impedance sensing system was utilized to kinetically analyze the cytotoxicity of different sizes as well as different concentrations of the materials by measuring the resistance of each electrode as the cells attach simultaneously and in real-time, a critical feature in the monitoring of cytotoxicity. To further enhance our results, each electrode was deposited with a gold salt in order to improve the reproducibility of each electrode in monitoring the cell attachment. An electrical impedance measuring biosensor to perform cytotoxicity assays on human lung fibroblasts and rainbow trout gill epithelial cells is made. Several metallic nanoparticles, carbon nanotubes and graphene

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nanosheets are tested. This method provides shorter run times, easier performance and more precise results. By measuring the impedance change when cells attach to the electrodes on the biosensing chip, real time kinetic effects of toxicity of the various materials are recorded. The biological and physical characterization of nanotoxic effects of engineered nanomaterials using the biosensing chip will also provide an alternative approach for setting standards for assessing toxicities of other nanomaterials. This system was able to provide a more rapid, efficient and straightforward method of measurement compared to the current method of incorporating the nanoparticles into a cell culture directly.

Surface plasmon resonance (SPR) is a quantum electromagnetic phenomenon arising from the interaction of light with free electrons at a metal-dielectric interface. At a specific angle or wavelength of light, the photons energy is transferred to the excitation of the free electrons oscillation on the surface. The change in the refractive index (RI) is influenced by the analyte concentration in the medium in contact with the metal surface. SPR has been widely used for the detection of gaseous, liquid, or solid samples. In this study, the use of a novel SPR module (PhotonicSys SPR H5) was tested for the detection of the stroke biomarker N-terminal pro-brain natriuretic peptide (NT-proBNP). NT-proBNP is secreted from the heart in response to increase in diastolic pressure of the heart. NT-proBNP is proven to be a good biomarker for stroke diagnosis, with sensitivity >90% and specificity >80%. However, there is still a need for a new diagnostics technique, mainly addressing assay specificity and set up. The PhotonicSys SPR H5 system, is a miniature fast and portable system, which can be easily integrated with other instruments and used in the field; therefore, it is attractive as a point-of-care sensor. The novelty in the technology is that the SPR substrates and the reading methodology. The system provides self-referenced measurement to compensate for drifts and provide a stable measurement. NT-proBNP detection was tested with two different types of SPR substrates having different top interacting surfaces (Au and SiO2), in water, buffer and plasma samples. In addition, specific detection was done by bondied anti-NT-proBNP antibody onto the SPR substrate. NT-proBNP was detected in a range of clinically relevant concentrations for stroke, from 0.1ng/ml to 80ng/ml. The sensor demonstrated a clinically relevant limit-of-detection (LOD) of 0.1ng/ml. In the case of silicon oxide substrate, the RI showed an increasing pattern with increasing concentrations. However, in the case of the metal substrate (Au-Ag), the RI showed a decreasing pattern with increasing concentrations. More detailed explanation for the difference in the two patterns will be given by examining further the interaction of NT-proBNP with each surface.

Porous, Ultrasoft, Magnetically-Stimulated Membranes for Biomimicry and Biosensors via 3D Printer Scaffolding

We will report how porous, elastic, and biocompatible membranes can be made by combining sheets from soft dendritic colloids (SDCs) with a magnetically-responsive, 3D printed silicone scaffold. The resulting multilayer structures could be used as tissue matrix surrogate scaffolds in magnetically-actuated cyclic strain bioreactors. SDCs are a new class of polymer aerogel material characterized by a branched corona of nanofibers spread out in all directions. They are produced in a scalable polyelectrolyte precipitation process under intensive shear. Their fractal, hierarchical structure enables remarkable adhesion and networking properties, mimicking the contact splitting effect seen in gecko leg adhesion. We show that SDC nonwovens composed of a thermoplastic polyurethane can be fabricated into porous, nonwoven membranes with morphological features similar to that of the branched, fibrous architectures comprising physiological tissues such as lung tissue. The SDC membranes are ultrasoft, with controllable moduli of physiological softness that can mimic both soft, healthy tissue and stiffer, diseased tissues characterized by stiffened fibers resulting from pathologies such as cystic fibrosis. These SDC membranes, combined with a new method of 3D printing of magnetically-responsive silicone mesh scaffolds, allow modulated, cyclic actuation of the material to predetermined strain values. The inclusion of these ultrasoft, porous membranes in a magnetically-actuated bioreactor setup will allow their facile, untethered, long-term actuation during cell growth to determine the effects of the scaffold’s mechanical properties on cell proliferation and viability in vitro for toxicological and human performance evaluations.
Thermotropic, hydrophobic liquid crystal elastomers have significant advantages of facile patterning, a variety of available monomers, and well-studied elastomer chemistries. These patternable elastomers can undergo high amounts of actuation strain, but these strains are typically not realized below 100-200 C, as determined by the liquid crystalline phase transition. To lower this actuation temperature to near body temperature, we use a 2-click thiol-acrylate/thiol-ene chemistry to copolymerize mesogens with isotropic monomers, which can shift the transition temperature and resulting actuation temperature from 105 C to 28 C. This control of phase behavior enables liquid crystal elastomers which can morph in response to contact with skin or warm tap water. Additionally, these low-temperature elastomers can be 3D printed, allowing structural freedom which is unfeasible in many other liquid crystal elastomer chemistries.

Alternatively, we can synthesize gels which respond to aqueous stimuli, such as pH, by building hydrogels from chromonic liquid crystals. We have synthesized the first hydrogel from chromonic liquid crystals which can be orderted through surface alignment and copolymerized with responsive monomers. By controlling the crosslink density of the gel with non-polymerizable chromonic precursors, we can polymerize gels ranging from ~10 kPa to ~300 kPa. The modulus of the gel is ~2x stiffer along the axis of molecular alignment, which guides anisotropic actuation in response to temperature and pH. This control over crosslink density not only allows for control over the magnitude of shape change but also allows us to synthesize gels similar to soft tissues with anisotropic mechanical properties.

With these strategies, we have taken steps towards the use of liquid crystalline polymers in biological applications. Both liquid crystal elastomers and liquid crystal gels have been used as substrates for mammalian cell culture to confirm the biocompatibility of these materials. By controlling the molecular orientation of these ordered gels and elastomers, we can potentially affect cellular behavior both statically by anisotropic modulus and dynamically by temperature-based or pH-based actuation.
**Supramolecular Biomaterials for Regenerative Medicine and Drug Delivery**
April 23 - April 25, 2019

**Symposium Organizers**
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Honggang Cui, Johns Hopkins University
Patricia Dankers, Technische Universiteit Eindhoven
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* Invited Paper

**SESSION SM05.01: Supramolecular Peptide Assemblies I**
Session Chairs: Eric Appel and Honggang Cui
Tuesday Morning, April 23, 2019
PCC North, 200 Level, Room 227 C

### 10:30 AM *SM05.01.01*
**Metabolite-Responsive Peptide Nanostructures**
Rain Ulijn1,2; Advanced Science Research Center, City University of New York, New York, New York, United States;
Department of Chemistry, Hunter College, New York, New York, United States.

Ligating systems derive their functions from the dynamic interactions of multiple components, they operate away from equilibrium, and rely on the continuous consumption of high energy metabolites (predominantly ATP) to sustain their existence. This differentiates living systems from synthetic materials, which are mostly static, simple in composition, and they do not consume energy to support their function. The active and multi-component properties of living matter gives rise to structures with rapid-response, selective and context-dependent dynamic functions that are currently not accessible to synthetic materials. The talk will cover our recent progress in the use of peptide ensembles to produce shape changing, metabolite consuming nanostructures. We will discuss: (i) our discovery approaches used to identify peptide ensembles which recognize metabolites, including ATP, (ii) the development of peptide ensembles with conformation-induced reactivity and (iii) the integration of modular functions of assembly, catalysis and metabolite recognition to form active materials.

**REFERENCES:**

### 11:00 AM SM05.01.02
**Nucleopeptide Assemblies Selectively Sequester ATP in Cancer Cells and Target Cell Nucleolus**
Huaimin Wang and Bing Xu; Brandeis University, Waltham, Massachusetts, United States.

Based on the recent near atomic structures of the PYRIN domain of ASC in the protein filament of inflamasomes, we rationally designed nucleopeptides to form supramolecular assemblies selectively sequester ATP in live cells and capable of delivery into cell nucleoli. We developed assemblies of nucleopeptides that selectively sequester ATP over ADP. Counteracting enzymes interconvert ATP and ADP to modulate the nanostructures formed by the nucleopeptides and the nucleotides. The nucleopeptides, sequestering ATP effectively in cells, slow down efflux pumps in multidrug resistant cancer cells, thus boosting the efficacy of doxorubicin, an anticancer drug. As the first example of assemblies of nucleopeptides that interact with ATP and disrupt intracellular ATP dynamics, this work illustrates the use of supramolecular assemblies to interact with small and essential biological molecules for controlling cell behavior. Moreover, the nucleopeptides accumulate preferentially at cell nucleolus, demonstrating the potential for nucleolus delivery for therapeutic benefits.

### 11:15 AM SM05.01.03
**STINGel—A Biomaterial-Based Drug Delivery Vehicle for Enhanced Cancer Immunotherapy**
David G. Leach1, Jeffrey Hartgerink1, Neeraja Dharmaraj2 and Simon Young2; Department of Chemistry, Rice University, Houston, Texas, United States; Department of Oral & Maxillofacial Surgery, University of Texas Health Science Center at Houston, Houston, Texas, United States.

Modern cancer treatment relies on the discovery and use of potent drug molecules, yet many drug therapies suffer from inefficient or unoptimized delivery methods, resulting in poor on-target efficacy and significant off-target effects. Our work focuses on the development of novel, biomaterial-based drug delivery vehicles that can be used to enhance the efficacy of existing therapies and treat challenging diseases such as cancer. Recent advancements in the field of immunotherapy have yielded encouraging results for the treatment of advanced cancers. For example, cyclic dinucleotides (CDNs) are a powerful new class of immunotherapy drugs known as STING (Stimulator of Interferon Genes) agonists, currently in clinical trials. However, previous studies of CDNs in murine cancer models have required multiple high dose injections, and improve survival only in relatively nonaggressive tumor models. Therefore, we are working to improve the efficacy of CDN immunotherapy by developing a novel biomaterial strategy we call “STINGel.” This was done through the use of Multidomain peptides (MDP) carrier vehicles, which can self-assemble into networks of nanofoamers that result in injectable hydrogels. Standard MDP hydrogels are biocompatible and can be loaded with various bioactive factors, facilitating cell growth in vitro and displaying complete cellular infiltration in vivo. This project studies the development of a delivery material to improve the efficacy of STING agonist anti-cancer immunotherapy, taking advantage of the charged domains of a lysine-based MDP hydrogel to achieve extended and localized drug release. STINGel has been shown to dramatically improve tumor survival over immunotherapy alone in a challenging murine cancer model, resulting in 6-fold higher survival after only a single intratumoral injection of CDN-loaded hydrogel. Continuing work seeks to develop second-generation delivery materials by synthesizing and studying new MDPs with different charge chemistries, and by characterizing their effects on drug release kinetics, immune response, and final tumor treatment efficacy. This project’s goals are to develop various new delivery biomaterials and better drug treatment methods, which will ultimately be translatable to the clinic.

### 11:30 AM *SM05.01.04*
**Self-Assembling Multidomain Peptide Nanofibers for Immunotherapy, Wound Healing and Other Biomedical Applications**
Jeffrey Hartgerink; Rice University, Houston, Texas, United States.

Multidomain Peptides (MDPs) are a class of self-assembling peptides which can form a nanofibrous gel under the proper environmental conditions which can be selected from...
cues such as pH and ionic strength. These hydrogels have convenient handling properties which allow them to be easily aspirated and subsequently delivered by syringe, even through exceptionally narrow-bore needles. Depending on the application, these hydrogel can be used loaded with small molecule drugs, proteins, cells or a combination of all these. However, the nanofibrous hydrogel can also be used unloaded where we have found that free of any bioactive agents it is rapidly infiltrated with cells in vivo and remodeled into highly vascularized tissue. One of the great advantages of MDPs are the ease with which they can be modified and tailored to a particular application. Over the past decade we have prepared over one hundred variants on this sequence and can now describe with confidence peptides that will assemble under acidic, basic and neutral pH, with or without complimentary salts and, most recently with and without charge on the nanofibers themselves. In this presentation I will discuss our general design criteria for self-assembling MDPs. I will also describe recent results related to their use in the treatment of a model of diabetic ulcers with and without bacterial infection. In this work we find that the innate regenerative ability of the hydrogel dramatically accelerates wound healing over a negative control as well as over a commercially available, and clinically prescribed, hydrogel. In a separate study I will describe the use of the MDP hydrogel as a small molecular delivery agent and compare it to commercially available hydrogels such as collagen, alginate, Matrigel and hyaluronic acid. Applying MDPs in a model of cancer immunotherapy we deliver a cyclic dinucleotide to dramatically improve the efficacy of this STING agonist in a challenging model of head and neck cancer.

References:

1:30 PM  Session SM05.02: Supramolecular Peptide Assemblies II

Supramolecular Peptide Immunotherapies—Effect of Material Structure on Immune Phenotype Yaoying Wu, Sean Kelly, Lucas Shores and Joel Collier; Duke University, Durham, North Carolina, United States.

Supramolecular peptide immunotherapies are receiving interest in a range of settings, from infectious diseases to cancer to chronic inflammation. One of the chief advantages of these materials is that their modular construction makes it possible, in principle, to adjust the strength and phenotype of the immune responses raised in different settings. Immune phenotype can be controlled grossly by the co-delivery of adjuvanting molecules, but here we sought to determine how fine differences in the nanostructures of supramolecular peptide materials also influence the strength and character of the immune responses raised. In this talk, the effect of various nanostructural aspects of supramolecular peptide materials, including size, stability, surface charge, and epitope content will be discussed. This work compared multiple self-assembling peptide systems, including beta-sheet fibrillizing peptides and alpha-helical fibrillizing systems that could be engineered to form assemblies of varying size. In mice, smaller assemblies were more capable of cross-presentation to stimulate CD8+ T-cell responses than larger assemblies, and the helical system generated stronger antibody responses for poor B-cell epitopes, likely because these materials contained T-cell epitopes within their assembly domains. In sublingual vaccination (under the tongue), peptides and peptide assemblies were found to be generally non-immunogenic, even when delivered with sublingual adjuvants; however, the addition of oligoethylene glycol moieties to the materials enabled them to elicit surprisingly strong immune responses. The necessity of achieving a carefully controlled strength and phenotype of immune response will be highlighted in the context of active immunotherapies against inflammatory cytokines such as TNF and IL-17, for which these materials continue to be in active development.

2:00 PM Session SM05.02: Molecular Mechanism of Alzheimer's Disease—Towards Prevention and Cure

Zoya Leonenko1,2,3, 1Department of Biology, University of Waterloo, Waterloo, Ontario, Canada; 2Department of Physics and Astronomy, University of Waterloo, Waterloo, Ontario, Canada; 3Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario, Canada.

Alzheimer’s disease (AD) is a neurodegenerative disease characterized by dementia and memory loss for which no cure or prevention is available. Amyloid toxicity is a result of the non-specific interaction of toxic amyloid oligomers with the plasma membrane. We studied amyloid aggregation and interaction of amyloid beta (1-42) peptide with lipid membrane using atomic force microscopy (AFM), Kelvin probe force microscopy and surface Plasmon resonance (SPR). Using AFM-based atomic force force spectroscopy (AFS) we measured the binding forces between two single amyloid peptide molecules. We demonstrated that lipid membrane plays an active role in amyloid binding and toxicity: changes in membrane composition and properties increase amyloid binding and toxicity. Effect of lipid composition, the presence of cholesterol and melatonin are discussed. We discovered that membrane cholesterol creates nanoscale electrostatic domains which induce preferential binding of amyloid peptide, while membrane melatonin reduces amyloid-membrane interactions, protecting the membrane from amyloid attack. Using AFS we find that novel pseudo-peptide inhibitors SG effectively prevent amyloid-amyloid binding on a single molecule level and thus can potentially prevent amyloid toxicity. These findings contribute to better understanding molecular mechanism of Alzheimer's disease and aid into developments of novel strategies for cure and prevention of AD.

References:

2:15 PM  Session SM05.02: Multidomain Peptide Hydrogel Accelerates Healing of Full-Thickness Wounds in Diabetic Mice

Nicole Carrejo, Amanda Moore, Tania Lopez Silva, David G. Leach, I-Che Li, Douglas Walker and Jeffrey Hartgerink; Rice University, Houston, Texas, United States.

Diabetes Mellitus is one of the most common metabolic disorders in the world, representing a significant health problem and economic issue. Approximately 15% of diabetic patients develop chronic wounds in their lower extremities due to complicating symptoms. Wounds in diabetic patients have relatively longer healing periods than normal wounds. Specifically, diabetic wounds exhibit delayed wound closure, prolonged inflammation, and are often infected with bacteria. The gold standard of treatment for diabetic patients with chronic wounds consists of debridement of the wound, infection control, offloading of weight, and patient education. Despite these efforts, chronic wounds frequently lead to amputation, an outcome that strongly motivates the development of new treatments. One approach to address these issues is to load cells, growth factors, or other biomolecules into scaffold materials to control release kinetics and achieve treatment localization. The difficulty here is the complex interplay between delivery material, diffusing soluble agents, and loaded cells. The wound healing process consists of a delicate sequential cascade of cell types and growth factors, and deviation from the proper sequence can adversely affect the
Many disease processes are driven by “undruggable” protein-protein interactions (PPIs) inside cells. In cancer, for example, tumor suppressor proteins are often inactivated by upregulation of their protein binding partners. Despite the promise of therapeutic peptides for disrupting PPIs, their delivery to and into cells remains a major obstacle to clinical translation. Peptides amphiphiles (PAs), a peptide conjugated to a hydrophobic tail, are one tool for facilitating intracellular peptide delivery. PAs self-assemble into micellar nanoparticles, protect peptides during delivery to diseased cells, and facilitate cell-uptake of peptides that would otherwise not be internalized. However, after internalization, PAs remain trapped in endosomes, which prevents them from reaching their cytoplasmic targets and reduces therapeutic efficacy. To facilitate their intracellular delivery, we have designed cleavable PAs to release therapeutic peptides after internalization and have explored strategies to facilitate their endosomal escape. We have explored this delivery system in two PPI systems frequently hijacked by cancer cells: the guardian of the genome (i.e. p53) and the gatekeepers of apoptosis (i.e. the BCL-2 family of proteins).

4:00 PM SM05.02.06
Self-Assembling Prodrugs Honggang Cui; Johns Hopkins University, Baltimore, Maryland, United States.

Covalent modification of a therapeutic agent represents an effective means to improve the drug’s pharmacokinetic profile for enhanced therapeutic outcomes. Incorporating the concept of molecular assembly into the prodrug design provides a new dimension for tailored synthesis of supramolecular medicine to address specific clinical needs. This self-assembling prodrug strategy uniquely and specifically exploits the self-assembling potential of therapeutic agents to achieve improved treatment efficacy. In this presentation, I will detail our rational design of monodisperse, amphiphilic anticancer drugs—which we term drug amphiphiles (DAs)—that can spontaneously associate into discrete, stable supramolecular nanostructures with a 100% drug loading. Our results suggest that formation of nanostructures provides protection for both the drug and the biodegradable linker from the external environment and offers a mechanism for controlled release.

4:15 PM SM05.02.07
Programmed Cell Death Instructed by Membrane-Interacting Supramolecular Assemblies Shantanu Sur1, Samuel Stupp2, Charlotte H. Chan3, Darren Sipes4 and Arielle Stoian1; 1Clarkson University, Potsdam, New York, United States; 2Northwestern University, Chicago, Illinois, United States.

The balance between charge and intermolecular hydrogen bonding is considered critical in determining the cellular effects of self-assembled peptide amphiphile (PA) materials. These two parameters have been tuned to induce cell membrane disruption, promote neuronal development, and amplify response to growth factors. To conjugate an alkyl tail at the C-terminus of the peptide in the PA, a lysine residue is commonly used as a linker. In this work, we show that the orientation of this lysine relative to the peptide chain and the alkyl tail plays an important role in determining PA’s ability to induce programmed cell death. When the alkyl tail is conjugated to the side chain amine of lysine linker, the resulting PA induced oncotic type of programmed death on cervical cancer cells, evidenced by loss of mitochondrial membrane potential, decrease in intracellular ATP level, and formation of giant blebs. Cell viability was rescued when the lysine orientation was reversed (the alkyl tail was attached to the primary amine) even though the nanostructure retained very similar morphology. Further investigation suggests that the oncosis could be triggered by an alteration in the cell membrane properties resulting from sequestration of cholesterol by membrane-associated PA nanofibers. Our results demonstrate how a subtle difference in the molecular design can be utilized to tailor the assembled nanostructure to elicit specific cell response.

4:30 PM SM05.02.08
Instructed-Assembly for Cell Morphogenesis and Mitochondrial Delivery Huiimin Wang, Hongjian He, Zhaoqianqi Feng and Bing Xu; Brandeis University, Waltham, Massachusetts, United States.

Context-dependent signaling, as a ubiquitous phenomenon in nature, is a dynamic molecular process at nano- and microscales, but how to mimic its essence using non-covalent synthesis in cellular environment has yet to be developed. Here we discuss two examples of instructed-assembly (iA) of a supramolecular phosphoglycopeptide (sPGP) as context-dependent signals for morphogenesis of cells; (2) enzymatic morphology/phase transition of isopeptides effectively delivery cargos to mitochondria in a cell selective manner. In the first case, while enzymes (i.e., ectophosphatasases) on cancer cells catalyze the formation of the filaments of the sPGP to result in cell death, damping the enzyme activity induces 3D cell spheroids. Similarly, relying on the ratio of stromal and cancer cells in a co-culture to modulate the expression of the ectophosphatase, the iA process enables cell spheroids. The spheroids act as a mimic of tumor microenvironment for drug screening. In the second case, consisting of DYKDDDDK (Flag, a substrate of enterokinase (ENTK)) as the branch and a phenylalanine rich short peptide as the backbone, the isopeptides (Mito-Flag) form micelles, which, upon the cleavage of the Flag catalyzed by ENTK, turn into a gel made of nanofibers. Entering cells mainly via clathrin mediated endocytosis, the micelles interact with the mitochondria having ENTK and high membrane potential. The mitochondrial ENTK cleaves the Flag of the isopeptides, thus turning the micelles to nanoparticles on the mitochondria. Mixing the Mito-Flags and cargos (drug molecules, proteins, and genes) allows the selective delivery of the cargos into mitochondria of cancer cells. These results provides a new way to control cell fates and to target organelles for biomedicine.
SESSION SM05.03: Poster Session: Supramolecular Biomaterials for Regenerative Medicine and Drug Delivery
Session Chairs: Eric Appel, Honggang Cui, Patricia Dankers and Matthew Webber
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

SM05.03.01
A Lipid Raft Modified Multifunctional Nano Gene Delivery System in Brain Targeting
Wei Wang1, Jianping Wang1, Qilong Wang1, Xia Cao1,2, Ximing Xu1 and Jiangnan Yu1
1 School of Pharmacy, Jiangsu University, Zhenjiang, China1, 2 Renal, Harvard medical school, Cambridge, Massachusetts, United States.

Glioma has become an extremely hazardous intracranial malignant tumor due to its high degree of malignancy and invasive growth, and there is no efficient way for therapy. Lipid rafts (LR) was discovered in the study of the biological membrane structure of a niche structure with special functions, and which could be an effective target for the antitumor agent in numerous malignancies. Here, we report a multi-functional nano-gene delivery system (MNDs), which wrapped carbon quantum dots and DNA in blood cell membrane and modified with lipid rafts sourced from U251 cells. The morphology of MNDS is characterized by SEM, TEM, and DLS, which showed that the modified MNDS had coated with lipid raft, and spherical size is around 100 nm. Compared with normal fibroblast, the results of in vitro had confirmed that LR modified MNDS could effectively target to U251. Besides, the modified MNDS can validly target brain sites after tail vein injection, which means the MNDS could successfully penetrate the blood-brain-barrier (BBB) in vivo. This new delivery system could potentially provide a new tragic for glioma differentiation, which could a new method for the therapy of cerebral disease therapy.

SM05.03.02
Coassembly of Enantiomeric Peptides Inside Mitochondria for Cancer Therapy
Ja-Hyoung Ryu; UNIST, Ulsan, Korea (the Republic of).

Homochiral assembly of amphiphilic peptides consisting either D- or L-enantiomers inside the living cells are emerging as an attractive strategy for different biological implications including therapeutic. However, less attention is given for the heterochiral assembly of peptides consisting both D- and L-isomers. Homochiral assembly containing both D- and L-isomers (racemates) could create wonders in their biological impact since the assembly of racemates often results in altered properties compared with enantiomers such as faster kinetics, higher mechanical strength and enzymatic stability. In here, we have monitored altered morphological and biological properties of a short peptide amphiphile, Mito-FF upon their co-assembly with mirror pair, Mito-ff. Mito-FF is an intra mitochondrial self-assembling peptide amphiphile, which induce cancer cell apoptosis followed by mitochondrial damage upon co-assembly inside mitochondrial fibrillation. Mito-FF upon co-assembly with Mito-ff induced thick fibrous bundle of diameter upto 100 nm, while enantiomers form fiber of diameter – 10 nm. The co-administration of Mito-FF and Mito-ff in the cell induced drastic mitochondrial disruption than enantiomers both in vitro and in vivo as a result of intra mitochondrial racemic co-assembly to form thicker Mito-rae fibrous bundles.

SM05.03.03
Receptor-Targeting Protein Nanocarriers for Potential Chemotherapy of Non-Muscle-Invasive Bladder Cancer
Ja Zhang, Mullapudi Sneha Sree, Juwita Rahmat, Ratha Mahendran, En-Tang Kang, Edmund Chiong and Koos Gee Nee; National University of Singapore, Singapore, Singapore.

Bladder cancer is the costliest cancer to treat, requiring long-term follow-up and repeat interventions, because almost 70% of patients with non-muscle-invasive disease will develop tumor recurrence, and about 25% will progress to the muscle invasive stage. One of the major shortcomings associated with current intravesical chemotherapy is the short residence time of the drug in the bladder since much of it is lost upon the first voiding of urine. Our research focus is on the development of protein drug nanocarriers in the form of albumin molecules (~6 nm) and nanoparticles (~100 nm) that can target and be readily taken in by tumor cells via targeting receptors that are highly expressed on bladder cancer cells. Peptides that target fibroblast growth receptor 3 (FGFR3), epidermal growth factor receptor (EGFR) and CD47 on human bladder tumor cells were designed and the uptake of these peptides by bladder cancer cells was investigated. The uptake of the peptide targeting CD47 was the highest followed by those targeting EGFR and FGFR3. Thus, our subsequent drug delivery study centered on protein nanocarriers conjugated with the CD47-targeting peptide, and loaded with drugs commonly used for non-muscle invasive bladder cancer therapy. Our in vitro experiments showed that within the exposure time expected for intravesical therapy (2 h), the killing of bladder cancer cells treated with these receptor-targeting drug-loaded nanocarriers was significantly enhanced (drug IC50 reduced by a factor of ~3 to >10) compared to the free drug or the drug-loaded non-functionalized nanocarriers. Thus, CD47-targeting drug-loaded protein nanocarriers are a promising candidate for intravesical chemotherapy against non-muscle-invasive bladder cancer.

SM05.03.04
Polymer Nanoparticle-Based Combination Therapy for the Treatment of Multi-Drug Resistant Bacteria and Biofilm Infections
Akash Gupta, Jessa Makabenta, Cheng-Hsuan Li, Ryan Landis, Friederike Schlüter and Vincent M. Rotello; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

The emergence of drug-resistance among pathogenic bacteria constitutes one of the paramount challenges to the human health worldwide. This threat is further exacerbated by biofilm-associated infections that are even more challenging to treat. Conventional antibiotic-therapies are ineffective due to their inability to penetrate biofilm matrix coupled with the rapidly growing number of antibiotic-resistant strains. Host-defence peptide mimicking synthetic polymeric have emerged as promising novel antimicrobials that can disrupt the microbial membrane and readily penetrate biofilm matrix. However, their lack of specificity towards mammalian hosts limits their widespread therapeutic application. Here, we report synergistic antimicrobial therapy using engineered polymeric nanoparticles with colistin antibiotic for combating MDR bacterial and biofilm infections. We observed an 8-16-fold decrease in antibiotic dosage in presence of polymeric nanoparticles to combat planktonic cells and eradicate pre-formed biofilms of multiple MDR species. The synergy observed on planktonic bacteria was attributed to the ability of NPs at (sub-lethal concentrations) to create small pores on bacterial membrane that increased influx of antibiotics inside the microbes. Moreover, antibiotic accumulation inside biofilms increased by ~3.5 times in presence of NPs, resulting in a synergistic effect to kill the constituent microbes. Overall, this strategy demonstrates the ability of polymeric NPs to minimize the side-effects caused by high doses of ‘lethal’ antibiotics while simultaneously rejuvenating the antibiotics rendered ineffective due to development of drug-resistance in bacteria.

SM05.03.05
Spatially Controlled Bioorthogonal Catalysis for Imaging and Drug Delivery
Riddha Das, Akash Gupta, Ryan Landis, Golen Y. Tonga and Vincent M. Rotello; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Bioorthogonal transformation of prodrugs and profluorophores using transition metal catalysts (TMC) offers a promising strategy for imaging and therapeutic applications. However, maintaining activity and controlling the localization of TMCs make their use in biomedical applications challenging. Here we report the engineering of nanoparticles of gold nanoparticles (AuNPs) with encapsulated TMCs (nanozymes) to provide specific intra- and extracellular localization. We used membrane-penetrating cationic nanoparticles for catalysis inside and ‘stealth’ zwitterionic particles to limit catalysis to outside of mammalian cells. Specific localization of nanozyme activity was demonstrated through bioorthogonal activation of profluorophores inside biofilms demonstrating potential for early detection of biofilm-associated infections. Taken together, these studies demonstrate a new level of spatial control for TMC-mediated bioorthogonal catalysis for diagnostic and therapeutic purposes.

SM05.03.06
Nerve/Osteoblast/Endothelium Multicellular System Based on Ultralong Hydroxyapatite Nanowires/Cellulose Multifunctional Biological Paper Promotes Bone Regeneration
Feng Liu; Crystal Materials Institute, Shandong University, Jinan, China.

Large segmental bone defect is a common clinical disease, which frequently leads to lifelong disability and seriously affect the quality of life of patients. Clinical transplantation of some bioactive scaffold materials has been applied to the treatment of bone defect. However, it remained a big challenge due to safety and efficacy concerns as well as the prohibitive cost. In general, severe bone injury is always accompanied by vascular injury and nerve injury, which still is a serious clinical challenge. Therefore, the new strategy is
not only to design a simple acellular biological scaffold, but also to construct a multicellular system to induce cell proliferation and differentiation, which can significantly accelerate tissue regeneration. As a bone component, hydroxyapatite is a common bioactive material, which is often applied in the repair of bone defects. Herein, we synthesized ultralong hydroxyapatite nanowires (>100 μm) and then prepared hydroxyapatite-cellulose flexible multifunctional biopaper. Growth factor bone morphogenetic protein (2-BMP-2) and nerve growth factor (NGF) were loaded in different areas of the paper. Adipose derived stem cells, endothelial cells and neural stem cells were seeded on different areas by cell printing technology. Along with the long-term release of growth factors, the induced cells were successfully differentiated into osteoblasts and nerve cells, which significantly promoted bone repair. This method provides a promising strategy for bone regeneration and bone tissue construction in vitro.

SM05.03.07
Jet Printing Organic Cocrystals from the Vapor Phase Siddharth Borsadia and Max Shtein; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Nearly half of newly discovered active pharmaceutical ingredients (APIs) suffer from poor dissolution in water. After finding a successful “hit” using high throughput screening methodologies, many promising APIs must undergo subsequent chemical modification to improve the dissolution behavior. Pharmaceutical cocrystals are of growing interest as a means of controlling the release of an active pharmaceutical ingredient (API) without modifying its molecular structure. Pharmaceutical cocrystals are typically defined as a combination of two organic compounds in solid form, held together by hydrogen bonds and simple stochiometries (e.g., 1:1, 1:2, etc. molar ratios) of API and coformer. By choosing an appropriate coformer, the dissolution behavior of the API (i.e. its concentration over time) can be controlled and even enhanced significantly over the pure form and can have many functional advantages. Current methods of creating pharmaceutical cocrystals, however, are limited by the necessity for a liquid solvent during synthesis, required post-processing, and compatible delivery methods. We have developed a novel, solvent-free method for synthesizing organic cocrystals. The method, organic vapor cocrystalization (OVCC), involves subliming the API and coformer into a carrier gas, followed by jetting the gas mixture onto a temperature-controlled substrate, where the organic materials condense to form the cocrystal film. As proof of concept, we demonstrate for the first time the synthesis of the cocrystal system of caffeine and succinic acid, whose isolation has not been previously obtained by conventional methods. X-ray diffraction and differential scanning calorimetry are used to confirm the presence of the cocrystal phase, while scanning electron microscope studies show that the cocrystal forms an elongated morphology comprised of long needles, whose length and orientation depend on process parameters. Because a liquid solvent is not needed, OVCC opens the door to new cocrystal systems and printing applications. The new OVCC process enables excellent process control and automation, and automation is highly scalable for the manufacturability of cocrystal products.

SM05.03.08
Encapsulation of Flavonoids and Triterpenoids Extracted from Cranberries in Peptide-Based Spheres Yasaman Hamedani, Catherine Neto, Milana Vasudev and Elvira Lou E. Evangelisti; University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States.

Nanoscale technologies and its applications in medicine for disease diagnosis, treatment and prevention, has gained considerable attention during the past decade. Nanomaterials have been widely used in drug delivery systems as nanotubes, nanomachines, nanofibers and nanomembranes since they can mimic or alter biological processes. Nanospheres have been widely investigated as transport vehicles due to the ease and efficiency of uptake in the cells. Peptide-based carriers are a promising candidate for drug delivery due to ease of synthesis via self-assembly, biocompatibility, biodegradability, and tuneable chemical structures. Such peptide-based nanospheres have the potential to be targeted for a specific organ as well as increasing the half-life in systemic circulation, enhancing bioavailability, improved retention time of the therapeutic molecules and intracellular penetration. In this study, the fabrication of peptide-based nanospheres by electrospinning technique have been demonstrated, and their potential as carriers for targeted delivery of cranberry extracted flavonoids such as proanthocyanidins, and triterpenoids such as quercetin and urso acid have been evaluated. For this purpose, triphenylalanine nanospheres containing the drugs have been fabricated using a coaxial electrospinning set-up. Probiotic bacteria such as L. acidophilus, L. casei and Akkermansia were also encapsulated in such micro-carriers to improve their viability in the gut and intestinal tract. The effect of encapsulation of bacteria in stimuli-responsive peptide-based carriers, which can assist with on-demand release and the co-encapsulation of proanthocyanidins and triterpenoids was studied to understand their influence on bacterial cell survivability. The self-assembly and secondary structure of the fabricated tripeptide spheres have been analyzed through SEM, FTIR, Raman and CD analysis. The morphology and chemical structure of drug and bacteria enclosed carriers have also been characterized. The nanospheres carriers have then been modified to be targeted specifically for colon cancer. The efficiency of the carriers was analyzed by observing the release behavior of each of the drugs with and without post crosslinking treatment. The extent of their delivery to cells and their influence on reduction in tumor cell proliferation has been analyzed. 

SM05.03.09
Fluorophilic-Lipophilic-Hydrophilic Poly-2-Oxazolines Block Copolymers as MRI Contrast Agents—From Synthesis to Self-Assembly Sergey Filipov1,2, Leonid Kabervo1, Bart Verbraeken1 and Richard Hoogenboom1; 1Harvard University, Cambridge, Massachusetts, United States; 2Institute of Macromolecular Chemistry, Prague, Czechia; 1Department of Organic and Macromolecular Chemistry, Ghent University, Ghent, Belgium.

This work focused on the synthesis and self-assembly of triphilic poly(2-oxazoline) triblock copolymers with high fluorine content towards our future aim of developing poly(2-oxazoline) MRI contrast agents. A highly fluorinated 2-substituted-2-oxazoline monomer, namely 2-(1H,1H,2H,2H-perfluorooctyl)-2-oxazoline was synthesized using the Grignard reaction. The polymerization kinetics of the synthesized monomer was studied and it was used for the preparation of triblock copolymers with hydrophilic 2-methyl-2-oxazoline, hydrophobic 2-ethyl-2-oxazoline and fluorophilic blocks by Cationic Ring-Opening Polymerization yielding polymer with low relatively dispersity (1.2-1.4). The presence of the blocks with the different nature in one copolymer structure facilitated self-assembly of the copolymers in water and dimethylsulfoxide as observed by dynamic light scattering, rytension transmission electron microscopy, and small-angle neutron scattering. The nanoparticle morphology is strongly influenced by the order and length of each block and the nature of solvent, leading to nanoparticles with core-shell structure as confirmed by small angle neutron scattering. The reported poly(2-oxazoline) block copolymers with high fluorine content have high potential for future development of MRI contrast agents.

SM05.03.10
A Bioinspired Platform to Deliver Neurotrophins to the Central Nervous System for Neural Regeneration Duo Xu and Yunfeng Lu; University of California, Los Angeles, Los Angeles, California, United States.

The central nervous system (CNS) plays a central role in the control of sensory and motor functions, and the disruption of its barriers can result in severe and debilitating neurological disorders. Neurotrophins are promising therapeutic agents for neural regeneration in the damaged CNS. However, their penetration across the blood–brain barrier remains a formidable challenge, representing a bottleneck for brain and spinal cord therapy. We developed a nanocapsule–based delivery system that enables intravenously injected nerve growth factor (NGF) to enter the CNS in healthy mice and non-human primate. The encapsulation of NGF is achieved by in situ polymerization, which grows a thin layer of polymer around individual NGF molecules, forming NGF nanocapsules. These nanocapsules can efficiently penetrate the blood–brain barrier and enter the CNS after intravenous administration via the endogenous neurotransmitter transport pathway. In pathological conditions, the delivery of NGF enables neural regeneration, tissue remodeling, and functional recovery in mice with spinal cord injury. This technology can be utilized to deliver other neurotrophins and growth factors to the CNS, opening a new avenue for tissue engineering and the treatment of CNS disorders and neurodegenerative diseases.

SM05.03.11
Supramolecular Polymeric Chemotherapy Based on cucurbit[7]uril-PEG Copolymer Hao Chen1, Yueyue Chen2, Han Wu1, Jiang-Fei Xu1, Zhiwei Sun1, Zhiwei Sun1, Xu Zhang3, Tianyi University, Beijing, China; 2Capital Medical University, Beijing, China.

For combining the advantages of supramolecular chemotherapy and polymer therapeutics, we developed a new strategy of supramolecular polymeric chemotherapy based on a water-soluble polymer (poly-CB[7]), with cucurbit[7]uril (CB[7]) embedded in its PEG backbone. A supramolecular polymeric complex was fabricated from poly-CB[7] and oxaliplatin, a typical anticancer drug, and displayed lower cytotoxicity to normal cells than oxaliplatin. In addition, the cytotoxicity of the oxaliplatin could be restored through competitive replacement of oxaliplatin from CB[7] cavity by spermine, which is overexpressed in the microenvironment of cancer cells. Interestingly, compared with pristine
oxaliplatin, the supramolecular polymeric complex showed higher cytotoxicity to cancer cells. The enhanced cytotoxicity may result from a combined effect of the release of oxaliplatin and the decrease of sperm in the microenvironment, as sperm is essential for cell growth and proliferation. Besides, the supramolecular polymeric complex also prevailed the pristine oxaliplatin on the long circulation performance in vivo. Therefore, by the interplay of polymer chemistry and supramolecular chemistry, the fusion of stability and adaptivity could be achieved, which may open new horizons for supramolecular chemotherapy.

SM05.03.12
pH-Induced Charge-Reversal Amphiphile with Cancer Cell-Selective Membrane-Disrupting Activity Yincheng Chang, Jiang-Fei Xu and Xi Zhang; Tsinghua University, Beijing, China.

Supramolecular chemotherapy aims to employ supramolecular chemistry to reduce cytotoxicity of cancer chemotherapy agents. To this end, a charge-reversal amphiphile exhibiting charge conversion from negative to positive induced by pH is designed. It selectively kills cancer cells through cell membrane disruption. This amphiphile comprising an alkyl chain and anionic headgroup of acid-labile β-carboxylic amide (C16N-DCA) was prepared. In the microenvironment of normal cells with pH 7.4, the negatively charged C16N-DCA exhibited considerably reduced cytotoxicity. However, in the acidic microenvironment of cancer cells with pH 6.5-6.8, the headgroup charge of C16N-DCA changed from negative to positive under hydrolysis of the acid-labile amide group. As a result, the generated cationic amphiphile displayed significant killing of cancer cells by disrupting their cell membranes. This strategy of supramolecular chemotherapy with concise design represents a new route of chemotherapy for anticancer strategies.

SM05.03.13
Multifunctional β-Cyclodextrin Macrocrosslinker-Based Self-Healable Hydrogels Showing High Mechanical Strength, Enhanced Stability and pH Responsiveness for Drug Delivery Daham Jeong, Chul-gu Kim, Yohan Kim, Seonmok Kim and Seunho Jung; Department of Bioscience and Biotechnology, Konkuk University, Seoul, Korea (the Republic of).

A novel multifunctional β-cyclodextrin macrocrosslinker-based self-healable hydrogel is developed by crosslinking β-cyclodextrin oligomer allyl ether (C[βCD–OM]AE), a β-cyclodextrin oligomer with allyl groups and quaternary ammonium groups formed from chlorohydrin and another epoxide, with adnamously guest units and acryl acid moieties. The covalent bonds between the allyl groups and hydrogel backbones are designed to increase the stability of supramolecular hydrogels without losing their self-repairing attribute by introducing a macrocrosslinker concept. This new hydrogel shows a trebling in the storage modulus and a high tensile strain up to 1590%. The tensile strength of the C[βCD–OM]AE@Ad hydrogel is more than double that of the monomeric βC hydrogel without cationic groups. The volume magnitude of the C[βCD–OM]AE@Ad hydrogel can be stably changed by swelling, and it can be expanded more than eight times on a shift in the pH from 1.2 to 7.4. In addition, the hydrogel shows good cytocompatibility. The C[βCD–OM]AE@Ad hydrogel also showed ibuprofen sustained-release property depending on the pH. This multifunctional βCD macrocrosslinker-based self-healable hydrogel designed to combine chemical links, the host–guest interactions of macrocrosslinkers, and electrostatic attractions could provide good stability, improved mechanical strength, and beneficial self-healing performances for further applications in a wide variety of fields, including biomedicine.

SM05.03.14
Aggar -Serin Blend Antioxidant Hydrogel Dressing for Chronic Wounds Suhela I. Tyeb1, Nitesh Kumar2, Ashok Kumar1 and Vivek Verma1; 1Biological Sciences and Bioengineering, Indian Institute of Technology Kanpur, Kanpur, India; 2Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, India.

Chronic wounds are difficult to heal and results in morbidity and economic burden on the patient. Hallmark of these wounds are prolonged inflammatory phase, poor collagen production, hampered angiogenesis, upregulation in reactive oxygen species (ROS) and matrix metalloproteases. In order to achieve good healing, it is desirable to address as many of the aforementioned issues as possible. Aggar-based hydrogels show the potential application as wound dressings owing to their high moisture retention, cytocompatibility, ease of fabrication, availability of raw materials and cost effectiveness. However, they do not exhibit substantial antioxidant property and enhancement in collagen production that are required in wound dressing materials for chronic wounds.

In this work, flexible agar-based hydrogel films were fabricated via solvent casting method. These films were incorporated with sericin protein to enhance the antioxidant property of dressing materials. These films showed an improvement in antioxidant property and collagen production that are required in wound dressing materials for chronic wounds.

Electrospinning is a versatile technique for producing composite micro-/nano-fibers from various functional materials. The properties of electrospray nanofiber membranes provide many versatile elements that can be excellent resources for biomedical applications, such as drug delivery, tissue engineering and wound healing. In addition, coaxial electrospinning produces core/sheath fibers that provides even more advanced features, such as (a) independent combination of two or more functional materials; (b) encapsulating functional molecules and their controlled release; (c) protection of incorporated drugs from the outer environment. In the initial stages of applying electrospinning fibers in the biomedical area, core/sheath fibers enabled the incorporation of two separate polymers into a single fiber in order to combine good mechanical properties from synthetic polymers and cell biocompatibility from biomaterials. In the past decade, coaxial electrospinning has become one of most popular techniques for developing novel drug delivery vehicles, enabling the controlled and sustained release of the drug from the fiber core. Moreover, multiple drugs can be individually incorporated into either the core or sheath layers (or both layers) enabling synergistic effect from two or more different drugs.

Moving beyond sustained release, “on-demand” release triggered by external stimuli has emerged recently. In this report, we present on-demand triggered release using stimuli-responsive materials, such as self-immolative polymer (SIP) and pH-responsive Eudragit polymers. We also introduce bio-responsive SMART nanofiber membranes for developing non-hormonal contraceptive devices. For triggered release by external stimuli, we have produced nanofibers with SIP in the sheath encapsulating core materials. In the absence of stimulus, no drug release is observed, whereas abrupt core release was observed upon SIP depolymerization is triggered by external stimuli. Controlled multi-pH response has also been demonstrated using core/sheath fibers made of two different Eudragit polymers. Core-sheath fibers made of Eudragit L 100 (EL100) core and Eudragit S 100 (ES100) sheath provide three-phase responses depending on environmental pH within physiological range. At pH < 5, no release was observed from either core or sheath layer. At pH within 5-6 range, while release from the sheath is minimal, the controlled release from the core can be obtained by adjusting the sheath thickness. For pH > 6, all core and sheath materials are quickly released. This three-phase responses within physiological range is very useful for targeted drug delivery in because the environment in human organs has different pH values. For all cases, due to the high surface-to-volume ratio of nanofiber membranes, their response rates to external stimuli or environmental pH is much quicker (> 25 x) than that of the cast film equivalent. Finally, we will introduce bio-responsive nanofiber devices for the contraceptive application without using any hormonal agent. The fiber device is made of HPMC and Carbopol 974P composite polymers. HPMC provides a mucoadhesive and highly viscous hydrogel network and Carbopol polymers provide the pH buffering capacity with high viscosity. Upon contact with seminal fluid (pH ~ 8), HPMC/Carbopol nanofiber membranes convert into hydrogel, providing a physical barrier by swelling, with a low pH value of ~4, which acts as a spermicidal agent. This non-hormonal bio-responsive contraceptive device is highly attractive for women’s health, providing excellent spermicidal performance without affecting user’s hormonal conditions.

SM05.03.16

Adorption Kinetics of Methylene Blue in Biocompatible Hydrogels for Drug Delivery Systems

Lucas Ribeiro, Renata Lang Sala and Emerson Rodrigues de Camargo; Chemistry, Federal University of Sao Carlos, Sao Carlos, Brazil.

The study of biomaterials based on injectable hydrogels has increased over the past years due to their potential medical application in non-invasive treatments for tissue engineering and drug delivery systems. These hydrogels can be adjusted to deliver drugs in vivo for long periods without activating the immune system. Thromsensitive hydrogels, as poly[N-vinylcaprolactam] (PNVCL), when heated above a determined temperature (called lower critical solution temperature, LCST) change from a state where the chains are swollen in an aqueous medium (by hydrophilic interactions) to a state in which they self-aggregate by predominant hydrophobic interactions [1]. In this transition, hydrogen bonds between the polymer chains and the water molecules break and the hydrogel aggregates expelling these molecules, creating a phase separation. By understanding the physicochemical aspects of the swelling-collapse transition, it is possible to evaluate the suitability of PNVCL as smart delivery systems [2]. PNVCL is biocompatible, facilitating its use as a biomaterial. In this way, PNVCL was synthesized by radical polymerization in the presence of azobisobutyronitrile (AIBN) initiator, dimethyl sulfoxide (DMSO) as solvent, for 4 h at 70 °C and N2 atmosphere. The hydrogel was purified using dialysis membrane to remove DMSO and monomers unreacted. The LCST and energies involved during the swollen to aggregate states were calculated from the analysis of a PNVCL aqueous suspension (1% m/v) by UV-vis spectrophotometry. The material changes from a transparent system to opaque when heated, allowing to be studied by its transmittance in different temperatures. The polymers synthesized showed a LCST of 33.6 °C, which results in the gel formation in the body temperature. The calculated enthalpy and entropy changes during the phase transition were 6000 kJ mol-1 and 20 kJ K-1 mol-1, respectively. The FTIR spectrum of PNVCL showed bands relatives to the functional groups C=O (1617 cm-1), C-H (2930 cm-1) and water adsorbed by the amide cyclic group (3300 cm-1). For applications as a drug delivery system, the hydrogels capacity to adsorb drugs was evaluated by varying the concentration of Methylene blue-MB (5, 10, 25, 50, 100 e 200 ppm). In this study, methylene blue was used as a model for hydrophobic drugs, which are usually difficult to be released in a controlled manner by hydrogels with a typical hydrophilic character. The advantage of PNVCL comes from its amphiphilicity, which hydrophobic groups interact with the medium and the hydrophobic chains agglomerated above LCST interact with the drug. PNVCL suspensions (5% m/v) in the presence of MB were heated at 37 °C for 5 min, centrifuged and the supernatant was measured by UV-vis spectrophotometry. Two adsorption mechanisms were tested: Langmuir and Freundlich. The best model fitted was Freundlich, which can be used to describe non-ideal systems with heterogeneous surface. The amount of dye adsorbed varying the PNVCL concentration (5,10 and 20% m/v) was also studied. The adsorption of 50 ppm MB was up to 40% and increased linearly with polymer concentration. Thereby, PNVCL can be a suitable injectable delivery system for hydrophobic drugs with different concentrations.

References:

SM05.03.17

Mesoporous Nanoparticles for Drug Delivery Applications

Shahjahan K. Chowdury1, SeungHyun Park1, Yong-il Park1 and Won Hyung Ryu2; 1Department of Advanced Material Science and Engineering, Kumoh National Institute of Technology, Gyeongbuk, Korea (the Republic of); 2School of Mechanical Engineering, Yonsei University, Seoul, Korea (the Republic of).

Recently, there have been increasing interests in mesoporous silica especially in the field of controlled drug delivery. It is increasingly important to control the degree of bioactivity and rate of bigradation of such mesoporous silica. In this study, mesoporous silica nanorods were obtained by filling the precursor sol derived from tetraethyloxysilicate(TEOS) into the columnar pores (20 nm – 200 nm) of anodic aluminum oxide (AAO) substrate, and their drug-performance were investigated. In addition, in order to use in intracranial drug delivery system, paramagnetic mesoporous nanoparticles having SPION (superparamagnetic iron oxide nanoparticle) cores were also fabricated by coating SPION nanoparticles with the same silica precursor sol which was used for the fabrication of the mesoporous silica nanorods. The porosity and biodegradation kinetics of the fabricated mesoporous nanorods and magnetic nanoparticles were analyzed using SEM, TEM, XRD, FTIR. The performance of the mesoporous silica nanorods as drug delivery carrier and intraocular drug delivery efficiency of the fabricated magnetic nanoparticles were evaluated.
Highly Functionalised Water-Soluble Fullerene Derivatives—Cage Size Affects Hierarchical Self-Assembled Structures

The natural extracellular matrix (ECM) is a highly dynamic, supramolecular structure composed of various bioactive molecules held together by specific interactions. The ECM directly interacts with cells and dictates cell behavior to a large extent. Our goal is to synthetically mimic this intricate natural system using supramolecular materials based on hydrogen bonding units. The dynamics of the supramolecular system is shown to be important in the presentation of bioactive epitopes to cells. By design, highly dynamic supramolecular fibrous particles decorated with cell adhesive RGD motifs were made and studied in solution. It was shown that these soluble particles interact with the cell surface, and that the dynamics of bioactive presentation is dependent on the method of supramolecular incorporation. Transient networks and hydrogels composed of similar molecules were shown to have slowed down dynamics, compared to the particles in solution. These hydrogels, when formulated in the right way, were able to enhance cell viability and adhesion. When highly robust solid materials were made using the same supramolecular motif, cell adhesion and migration could be tuned. However, the ECM displays a plethora of bioactive peptide signals. Therefore, a high throughput screening approach was taken using a design of experiments set up, to investigate a library of natural ECM proteins as coatings, and a synthetic library of ECM peptides supramolecularly incorporated as additives in the base material. It was found that the several sequences and/or combinations outperformed others, showing the importance of the high throughput screening approach. The proposal that both the dynamics and presentation of bioactive sequence determines cell behavior is currently being investigated. In this way we aim to make steps towards the design of a synthetic ECM analogue.

Dissipative Supramolecular Materials with a Tunable Lifetime

Most biological materials exist in non-equilibrium states driven by the irreversible consumption of high-energy molecules like ATP or GTP. These energy-dissipating structures display a plethora of bioactive peptide signals. Therefore, a high throughput screening approach was taken using a design of experiments set up, to investigate a library of natural ECM proteins as coatings, and a synthetic library of ECM peptides supramolecularly incorporated as additives in the base material. It was found that the several sequences and/or combinations outperformed others, showing the importance of the high throughput screening approach. The proposal that both the dynamics and presentation of bioactive sequence determines cell behavior is currently being investigated. In this way we aim to make steps towards the design of a synthetic ECM analogue.

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We and others have thus set out to explore the use of dissipative self-assembly for the use of supramolecular (bio)-materials.[1-7] In this work, we will design criteria for dissipative supramolecular materials. I will focus on our recently described system and its application as a vehicle that can control cellular uptake, or deliver drugs.

References:

The Design and Application of Dissipative Supramolecular Materials

Marta Tena-Solsona, Raphael K. Grötsch, Caren Wanzke, Benedikt Rieß, Patrick Schwarz, Fabian Schnitter and Job Boekhoven; TUM - Chemistry Department, Garching, Germany.

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References:

Highly Functionalised Water-Soluble Fullerene Derivatives—Cage Size Affects Hierarchical Self-Assembled Structures

Ilija Rasovic1,2, Alba Piacenti3, Sonia Contera1 and Kyriakos Porfyrakis1
1University of Birmingham, Birmingham, United Kingdom; 2Materials, University of Oxford, Oxford, United Kingdom; 3Clarendon Laboratory, Department of Physics, University of Oxford, Oxford, United Kingdom.

The fullerenes are a unique carbon allotrope family that boast many desirable properties for therapeutic and diagnostic applications in nanomedicine, such as improved magnetic resonance imaging (MRI) contrast agents, photodynamic therapy (PDT) agents and enzyme inhibitors, for example. These highly hydrophobic cages, however, must be modified in order to enter the human body safely and effectively, and avoid rejection. One such method is covalent functionalisation: the covalent attachment of water-solubilising groups to the fullerene cage.

PEGylation (the covalent attachment of polyethylene glycol (PEG) chains) is often used to functionalise nanoparticles with the aim of negating rejection by the body. Inspired by this, but looking to reduce the dominance of the long PEG chain, we functionalised fullerenes C60, C70, C84 and C90 with triethylene glycol based chains. We have characterised the

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resultant molecular structures. Strikingly, depending on the size of the fullerene cage, these molecular building blocks self-assemble in aqueous solution to give complex hierarchical structures with porous architectures defined by a network of tubular fibrils. The mechanical properties of these hydrogels have been investigated using atomic force microscopy. Not only are these findings of interest to the study of the fundamentals of self-assembly processes, but the resultant structures hold great promise for the utility of fullerenes in the field of nanomedicine.

1:30 PM *SM05.05.01
Macromolecular Therapeutics

Multi-drug resistant diseases are one of the biggest challenges society is facing in the domain of healthcare. Contraction of a multi-drug resistant disease, whether through a microbial infection or the loss of chemotherapeutic effectiveness, results in an extremely poor patient prognosis given the severely limited treatment options. The rapid resistance development in microbes, for instance, has completely eviscerated the current antimicrobial drug pipeline. The resistance development of a variety of cancer cell lines has rendered treatment with a single therapeutic agent completely ineffective. Instead, chemotherapeutic treatments must rely on a bevy of chemotherapeutic agents and chemosensitizers to achieve remission, most often at the cost of the patient’s well-being, owing to significant toxicity.

Traditional, small-molecule drug therapy usually targets highly specific cellular processes or interactions, enabling resistance development through simple mutations in the pathogen’s genome. In contrast, macromolecular therapeutics consist of polymeric assemblies that exhibit selective but non-specific interactions with the pathogen, making resistance development extremely difficult. In fact, macromolecular therapeutic agents developed at IBM have shown no resistance development in the treatment of bacteria and viruses, in preliminary in vitro studies. Additionally, these agents have been found to be highly effective against drug-resistant bacteria and cancer cell lines, while maintaining very low toxicity towards healthy cells. Given these impressive features, macromolecular therapeutics hold significant promise for disease treatment.

2:30 PM BREAK

SESSION SM05.06: Supramolecular Hydrogels

Glioblastoma multiforme (GBM) is the most common primary cancer in adults and one of the most aggressive cancers with extremely poor survival statistics owing to high rates of disease recurrence. GBM infiltrates the brain tissue diffusely making complete surgical excision impossible. Current standard of care involves surgical resection of the tumour, concomitant radiotherapy and alkylating chemotherapy, followed by adjuvant chemotherapy. Chemotherapeutic choices are limited on account of most drugs’ poor propensity to cross the blood brain barrier. Systematic treatment with unspecified concentrations of chemotherapy is ineffective and risks adverse side effects. A localised and sustained delivery for various therapeutic applications including diabetes, vaccine development, immunotherapy, and CRISPR-Cas based gene editing. In this talk, I will discuss the design, synthesis, biological studies, and biomedical applications of our new vectors.

3:30 PM *SM05.06.01
Overcoming the Blood-Brain Barrier—Post-Resection Drug Delivery to Glioblastoma Multiforme Using Supramolecular Hydrogels

Zhibin Guan; University of California, Irvine, Irvine, California, United States.

Various RNAs, such as siRNA, microRNA, and mRNA, play pivotal roles in biological functions and have gained increasing importance for therapeutic applications. However, the lack of safe and efficient delivery vehicles remains the major challenge to RNA-based therapeutics. Our lab designs both small molecule and polymer-based molecular carriers for safe and efficient delivery of both short and long RNAs into cells. Using natural building blocks such as amino acids, we have developed dendronized bolaamphiphiles and polypeptides that are biocompatible, biodegradable, and highly efficient for RNA delivery. Our systematic investigation into structure–property relationships revealed important correlations between molecular design, self-assembled nanostructure, and biological activity. Through collaborations with biomedical researchers, we further investigate RNA delivery for various therapeutic applications including diabetes, vaccine development, immunotherapy, and CRISPR-Cas based gene editing. In this talk, I will discuss the design, synthesis, and the biological and biomedicinal applications of our new vectors.

References:

Through dynamic supramolecular recognition, it is possible to create materials rationally designed beginning at the molecular level with specific, dynamic, and tunable non-covalent interactions. Certain benefits to this approach are precise control of composition, improved routes for targeting drugs, and new strategies to create materials that respond to a variety of stimuli with concomitant changes in their properties. The modularity of supramolecular interactions also facilitates opportunities to combine multiple payloads within a single delivery platform, as well as a route to the facile incorporation of specific targeting motifs that enable recognition in complex biological milieu. Using macrocyclic host-guest recognition, dynamic and tunable heterodinumeric interactions enable precise control over the properties and availability of small molecule and protein drugs. This includes the ability to design new materials with affinity-directed dynamics, stimuli-responsive properties, or user-directed changes in mechanical properties. Furthermore, the ability to precisely tune affinity leads to a spectrum of different dynamics in topologically identical materials, as well as facilitating recognition even in complex or contaminated environments. By leveraging this affinity axis, a new route to precisely target therapies may also be achieved. We are very excited about this approach to creating new functional biomaterials through engineered supramolecular interactions, and will highlight these advances across several material platforms.

The "printing," or layer-by-layer extrusion, of cell-laden hydrogels results in the fabrication of 3D tissue-like structures. These fabricated tissues have potential applications in regenerative medicine and as in vitro tissue prototypes for drug screening. Bioinks for 3D bioprinting of synthetic tissues must fulfill three criteria: they must have rheological properties appropriate for extrusion printing, they must be cyto-compatible during the printing process, and they must include biological cues to control cell behavior after printing. Here we report on a recently developed family of bioinks that meet these requirements and can be further customized to achieve a range of mechanical properties. These hydrogel-based bioinks are produced from blends of engineered recombinant proteins and peptide-modified, naturally occurring biopolymers such as alginate. These materials undergo two-stages of crosslinking: (i) weak, peptide-based, supra-molecular assembly to homogeneously encapsulate cells in a shear-thinning hydrogel within the ink cartridge and (ii) stimuli-responsive crosslinking post-printing to rapidly stabilize the construct. Benefits of this two-stage crosslinking strategy include the prevention of cell sedimentation within the ink cartridge, mechanical shielding of the cell membrane from damaging extrusion forces during printing, rapid post-print self-assembly within an aqueous bath that prevents cell dehydration, and fine-tuning of the printed scaffold mechanical properties for optimal cell-matrix interactions. We demonstrate that tuning of the hydrogel material properties can be used to identify bioinks suitable as scaffolds for the large-scale expansion of neural stem cells.

9:45 AM *SM05.07.02 Supra-Molecular Hydrogels as Custom Bioinks Sarah Heilshorn; Stanford University, Stanford, California, United States.

The "printing," or layer-by-layer extrusion, of cell-laden hydrogels results in the fabrication of 3D tissue-like structures. These fabricated tissues have potential applications in regenerative medicine and as in vitro tissue prototypes for drug screening. Bioinks for 3D bioprinting of synthetic tissues must fulfill three criteria: they must have rheological properties appropriate for extrusion printing, they must be cyto-compatible during the printing process, and they must include biological cues to control cell behavior after printing. Here we report on a recently developed family of bioinks that meet these requirements and can be further customized to achieve a range of mechanical properties. These hydrogel-based bioinks are produced from blends of engineered recombinant proteins and peptide-modified, naturally occurring biopolymers such as alginate. These materials undergo two-stages of crosslinking: (i) weak, peptide-based, supra-molecular assembly to homogeneously encapsulate cells in a shear-thinning hydrogel within the ink cartridge and (ii) stimuli-responsive crosslinking post-printing to rapidly stabilize the construct. Benefits of this two-stage crosslinking strategy include the prevention of cell sedimentation within the ink cartridge, mechanical shielding of the cell membrane from damaging extrusion forces during printing, rapid post-print self-assembly within an aqueous bath that prevents cell dehydration, and fine-tuning of the printed scaffold mechanical properties for optimal cell-matrix interactions. We demonstrate that tuning of the hydrogel material properties can be used to identify bioinks suitable as scaffolds for the large-scale expansion of neural stem cells.

9:45 AM BREAK

10:15 AM *SM05.07.03 Materials Science for Regenerative Biology Samuel Stupp; Northwestern University, Evanston, Illinois, United States.

One of the grand challenges for science in this century is to create strategies to regenerate parts of the human body in order to achieve longer “healthspans.” Materials science has a central role to play in this quest, which is both a highly desired and critical societal outcome given shifting demographics. The ultimate role, but not the only one, of materials in regenerative biology is to act as a bioactive medium with finite half-life that traffics signals in dynamic fashion. This in fact imitates the function of extracellular matrices as tissues develop or repair after injury, and requires molecular design of soft materials to directly activate signaling pathways via cell receptors or protein signals such as growth factors. This lecture will describe a broad platform of supramolecular biomaterials built with a toolbox of peptides, peptide amphiphiles, glycans, and nucleic acids that exhibit various forms of dynamic bioactivity toward neural or musculoskeletal cells. In one example it is possible to switch biological signals on and off through external cues, and in another one there is capacity in the material to adapt to the living structure for optimal signaling. In a third example an unprecedented soft material that exhibits reversible self-assembly of superstructures is found to modulate the phenotype of cells involved in tissue repair.

10:45 AM *SM05.07.04 Kidney Organoid Encapsulation in Static vs Dynamic Cross-Linked Supramolecular Hydrogels for Organoid Growth Floer A. Ruiter, Thomas Geuens, Shahzad Hafeez, Antonio Feliciano, Clemens A. van Blitterswijk, Vanessa LaPointe and Matthew Baker; MERLN Institute for Technology-Inspired Regenerative Medicine, Maastricht University, Maastricht, Netherlands.

Induced pluripotent stem cells (iPSCs) differentiated to a mixture of kidney cell types are observed to rearrange into kidney nephron-like structures when aggregated, spotted and cultured in a media/air interface. Although kidney like structures were observed, organoid growth is limited. No further growth or rearrangement was observed after 18 days in a media/air interface cell culture. Moreover, preliminary results within our group showed overexpression of extracellular matrix (ECM) proteins, which is due to a fibrosis reaction. Here we hypothesized a possible need for a 3D environment, which mimics the in vivo surrounding matrix of the developing kidney in the fetus. Hence, the use of supramolecular hydrogels.

Conventional supramolecular hydrogel cross-linking methods mostly rely on static covalent chemistry, such as thiol-ene chemistry. Although these hydrogels show similarities to the in vivo ECM structural characteristics, they do not mimic the dynamic behavior of the natural ECM. Cells within the natural ECM are constantly stimulated by physical and chemical cues, which change over time. For example, the repair of injured tissue occurs in multiple stages. Initial provisional matrix deposition is at the injured tissue side where matrix modification restores the tissue. However, small difference in environment cues can result in excessive secretion of collagen by the cells, which subsequently results in fibrosis or scar tissue. The dynamic cues and interactions of matrix composition, biochemical molecules and matrix mechanics all play a significant role to the cellular behavior and induced pathways to healthy or diseased tissues. Therefore, there is a need for scientists to design the hydrogel that mimics this dynamic behavior beside static structural composition.

New dynamic visco-elastic cross-linked supramolecular hydrogels of reversible covalent chemistry offer a novel approach to mimic the natural dynamic ECM behavior. Within our lab we observed a significant different in hydrogel stiffness, stress relaxation time and self-healing characteristics with different cross-linkers. This shows the possibility of tuning these materials for the desired dynamic behavior for the required cellular response.

Here we encapsulated the formed kidney organoids in the design reversible covalent chemistry cross-linked supramolecular hydrogels. Organoid cell arrangement, ECM expression, proliferation, and metabolic response were investigated in these designed hydrogels. These results were compared with to the encapsulation of organoids in a conventional thiol-ene static covalent cross-linked hydrogel.


11:00 AM SM05.07.05 Covalent-Supramolecular Polymer Hybrids for Cartilage Repair Jacob A. Lewis1, Mark McClendon1, Brett Nemke2, Yan Lu1, Mark Markel2 and Samuel Stupp3, 1; 1Department of Biomedical Engineering, Northwestern University, Evanston, Illinois, United States; 2School of Veterinary Medicine, University of Wisconsin–Madison, Madison, Wisconsin, United States; 3Simpson Querrey Institute, Northwestern University, Chicago, Illinois, United States; 4Department of Materials Science and Department of Chemistry, Northwestern University, Evanston, Illinois, United States.

Articular cartilage lacks the intrinsic ability to regenerate following injury or disease. Biomaterials scaffolds can improve cartilage healing by supporting cell infiltration and guiding new matrix deposition, yet these materials must withstand dynamic shear in the articulating joint. Transforming growth factor β-1 (TGFβ-1) binding peptide amphiphile (PA) matrices have been shown to improve cartilage healing in a lapine model; however, these materials lacked the mechanical integrity necessary for use in load-bearing large-animal joints. To improve material retention, we developed a PA-hyaluronic acid (HA) hybrid material, which improved the mechanical toughness of scaffolds. Combining these two materials formed a biocompatible gel with a highly porous microstructure containing bundled supramolecular polymers. Because of its improved mechanical properties, the material was well retained in shallow osteochondral defects in the load-bearing knee condyle. Four weeks following implantation, joints treated with TGFβ-1 loaded scaffolds revealed an improved level of tissue infiltration and integration with surrounding cartilage relative to control defects treated with only the growth factor alone. The observed improvements early in the healing process suggest the possible use of these covalent-supramolecular polymer hybrids as scaffolds for cartilage repair.

11:15 AM SM05.07.06 Evaluating and Designing BTA Supramolecular Hydrogels for Viscoelastic 3D Cell Culture Shahzad Hafeez1, Nicholas M. Matsumoto2, René P. Lafeur2, Egbert W. Meijer2 and Matthew Baker2; 1Department of Complex Tissue Regeneration (CTR), MERLN Institute, Maastricht University, Maastricht, Netherlands; 2Institute of Complex Molecular Systems (ICMS), Eindhoven University of Technology, Eindhoven, Te Netherlands, Eindhoven, Netherlands.

The extracellular matrix (ECM) is the non-cellular component present within all tissues and provides essential biological and mechanical cues required for tissue growth. Traditional synthetic covalent hydrogels (a network of hydrophilic polymers) have been investigated for 3D cell culture and probing cell-matrix interactions as they mimic the
mechanics of soft tissues and support cell adhesion. However, these hydrogels are elastic and lack the viscoelasticity found in native ECM and soft tissues and can only allow tissue formation via degradation, since they are built from covalent bonds. To overcome these limitations, hydrogels with reversible crosslinks are developed which could respond to cell stresses by rapidly breaking and reforming the bonds while maintaining uniform biophysical properties.

In our lab, we are working with 1,3,5-benzenetricarboxamide (BTA) supramolecular hydrogels. BTA molecules stack over each other through 3-fold hydrogen bonding and hydrophobic interactions to form long self-assembled BTA fibres, resulting in the hydrogel. BTAs are of interest for us owing to their cell-relevant timescales, protein-like fibrous structures and the ease of adjusting viscoelastic properties by controlling interactions at the molecular level. In addition, these gels exhibit injectability, showing a potential for bioprinting, and can serve as a platform for the generation of spatiotemporal dynamic co-cultures.

For cell viability, cultured cells within gels were stained with calcinein-AM and ethidium homodimer-1 and imaged using fluorescence microscopy. Minimal cytotoxicity was observed over 7 days. To be more quantitative, an absorbance-based LDH and CyQUANT assays were carried out. LDH assay showed approximately 10% dead cells and results are comparable to algin control sample, CaCl₂ crosslinked. The CyQUANT assay showed that cell number fairly stayed constant and gels did not enhance the proliferation. Interestingly, chondrocytes aggregation within gels were observed over time which was visualized with actin and nuclei staining. Currently, cell culture experiments are being carried out to investigate cartilage matrix formation by chondrocytes within BTAs hydrogels with varying viscoelastic timescales.

Furthermore, to expand the current BTA hydrogelator library (with different architectures) work was carried out towards desymmetrization of BTAs; a penta-fluorophenol BTA synthon (BTE-F,Ph) has been synthesized and desymmetrized using hexylamine as a model reaction. This work enables the creation of a small library of hydrogels with varying dynamicity and viscoelasticity that can help in developing a better understanding of cell-ECM interactions and directing cell fate.

11:30 AM *SM05.07.07
From Dynamically Crosslinked Hydrogels to Tunable Bioinks for 3D-Printed Tissue Engineering Constructs Matthew Baker, MERLN, Maastricht University, Maastricht, Netherlands.

Statically crosslinked hydrogels poorly recapitulate the complex and responsive behavior of a cell’s native extra cellular matrix (ECM). Cells have a difficult time growing, migrating, and fusing to form tissue within a densely crosslinked covalent hydrogel, yet covalently crosslinked hydrogels are the most widely used material for 3D printing of cell laden hydrogels (bioinks). Consequently, in order to create more complex and biomimetic 3D tissue engineering constructs, there is a noticeable need for the creation and use of dynamically crosslinked hydrogels within biofabrication and 3D printing.

Recently, our lab has developed both supramolecular and dynamic covalently crosslinked hydrogels which show high cell viability upon encapsulation, tunable network dynamics and mechanical properties, and exhibit self-healing, injectability, and 3D printability. In this talk, I will mainly focus on the dynamic covalent crosslinked hydrogels based on imine type crosslinking. These imine cross links are dynamic under physiologic conditions, resulting in appreciable on/off rates depending on the molecular structure of the crosslinker. Furthermore, these hydrogels are easily functionalized with biological cues using oxime ligation strategies. Several cell types (HDF, ATDC5, pancreatic islets) show good cell viability within these hydrogels. We observe noticeable changes in cellular function (proliferation, morphology, etc.) depending on the dynamics of the hydrogel formulation, enabling the matching of network dynamics with the desired cellular response. These hydrogel formulations also show good 3D printability, allowing the creation of spatially defined cell-laden constructs with enhanced function (as compared to other covalent bioinks).

These developed hydrogels represent new classes of dynamic bioinks for 3D printing and the construction or large tissue engineering constructs. The ability to fabricate appreciable size and spatially defined objects with biomimetic network dynamics enables the creation of complex multicellular constructs that can facilitate inter-cellular communication. Current efforts in the lab are focused on using these dynamically remodelable networks to study the interactions of cells and migration through reversible networks in complex geometries.
Hydrogel Inks for 3D Printing: Eugenia Kumacheva; Chemistry, University of Toronto, Toronto, Ontario, Canada.

Man-made nanofibrillar hydrogels have recently emerged as a new class of bionimetic materials that reproduce the filamentous nature and properties of in-vivo extracellular matrices, act as scaffolds for three-dimensional cell culture and tissue engineering, and offer interesting properties in actuation and soft robotics. Our group has developed new “inks” for 3D printing of hydrogels that are derived from cellulose nanocrystals and different types of polymers. These inks offer a number of useful properties, including their shear thinning behavior, the biocompatibility of the resulting hydrogels and the capability to fine-tune hydrogel composition, structure and physical properties in a throughput manner.

11:30 AM *SM06.01.03
Optically Camouflaged Microgel In Water—Prescribed Pattern Transformation in Swelling and Thermochromic Effects
Nicholas Fang and Xinhao Li; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Amazing capabilities of structural coloration and camouflage in marine animals such as cephalopod has inspired intensive study of smart materials and functional coatings. How do we gain control over optical and acoustic response using such soft and switchable microstructure of hydrogel? In this talk, we will present some simple analytical model that outline the design strategies of these transparent microgels. Our model suggest that inhomogeneous stress develops as the gel swells under mechanical constraints, which gives rise to spontaneous buckling instability without an external force. We will also demonstrate a new type of thermochromic coating using co-polymerized pNIPAm–AEMA hydrogel microparticles. The light blocking mechanism is clearly elucidated by applying Mie scattering theory, which predicts the scattering efficiency in a broad solar spectrum. The cross-link density and size of the microgel particles are manipulated to deliver prominent performance in both modulating solar thermal and visible light spectrum, which is unachievable by any thermochromic counterparts. We further discuss the potential applications agile and transparent actuators and robots formed hydrogel in water.

1:30 PM *SM06.02.01
Jamming and Rheology of Microgels—The Role of Particle Architecture
Maddalena Mattioli, Sarah Goujard and Michel Cloitre; ESPCI Paris, Paris, France.

At high concentration, microgels form glassy materials which behave as weak elastic solids at rest but yield and flow at high stresses. These materials are basic components of viscoelastic formulations used as high-performance coatings, solid inks, ceramic pastes, textured food, and personal care products. Synthetic chemistry offers a panel of strategies to tune the internal architecture of microgels and their interactions, which involve elastic repulsion and attractions of different origins. An important question concerns the relation between the particle elasticity, the phase diagram, the nature of the liquid to solid transition, and the macroscopic rheology [1].

Microgel elasticity can be tuned by varying the crosslink density, which appears to be one of the key parameters that determine the phase diagram and the rheology of microgel suspensions. Highly crosslinked microgels exhibit well-defined glass and jamming transitions and cross from liquids to entropic glasses and jammed glasses when the volume fraction is increased [2]. In the jammed glass regime, the flow properties exhibit universal properties. The macroscopic rheology is well described by a micromechanical model where microgels are described as purely elastic particles interacting under the combined action of elastic repulsive forces and viscous drag forces [3]. Weakly crosslinked microgels behave very differently. They solidify above a well defined volume fraction but the glass and jamming transitions can no longer be disentangled. Yielding is now time dependent and the flow curves exhibit distinct scaling properties.

These behaviors are representative of two universality classes of soft particles where the flow properties are controlled by the dynamics of the elastic cages formed by interlocked neighboring particles and the viscoelastic deformation of individual particles, respectively.


2:00 PM *SM06.02.02
Searching for Universal Features of Soft Deformable Colloids—A Comparison of the Rheology of Dense Microgel and Star Polymer Suspensions
Leo Gury, Michel Cloitre and Dimitri Vlassopoulos; 1 FORTH, Crete, Greece; 2 ESPCI, Paris, France.

Dense microgel suspensions have both been shown to exhibit a thermal glass-to-jammed glass transition, characterized by large yield stress and linear dependence of plateau modulus on concentration, as well as other fine differences in flow curves [1]. There appears a consensus suggesting that shape adjustment in the highly concentrated regime is at the origin of jamming [3]. On the other hand, hairy particles represent a distinct class of soft colloids, being essentially the counterpart of microgels, with the additional feature (and degree of freedom) being their dangling arms [4]. Hence, a natural question that emerges concerns the role of internal microstructure on the dynamic properties of soft colloids and in particular the possible glass to jamming transition at high concentrations. Here, we address this challenge by systematically investigating highly concentrated suspensions of well-characterized microgels and multimer star polymers. Whereas both types of particles are able to shrink and deform under the action of osmotic pressure, star polymers can also interpret their arms and, moreover, can be investigated throughout the entire concentration regime up to the dry melt state. We show that the difference in the internal particle microstructure is reflected in distinct rheological signatures of these soft colloids. We focus on linear and nonlinear rheological shear measurements and analysis with additional support from dynamic light scattering, and attempt at providing a generic guidelines for tuning the flow properties of soft colloids via knowledge of their microstructure. Subtle differences in flow curves and associated velocity profiles are critically discussed and linked to the different features that dictate particle softness. We show that these distinct universality classes of soft colloids possess flow properties with generic features which can be tailored at molecular level.


2:30 PM SM06.02.03
Passive Microrheology Analysis of Sol-Gel Processes by Diffusing Wave Spectroscopy
Matt Vanden Eynden, Roland Ramsch, Giovanni Brambilla, Pascal Bru and Gerard Meunier; 1 Formulaction, Inc., Worthington, Ohio, United States; 2 Formulaction, Toulouse, France.

Passive microrheology is a powerful tool to study gels and their formation. Passive microrheology consists of using micron sized particles to measure the local deformation of a sample resulting from the thermal energy, the Brownian motion. Our technique is based on Diffusing Wave Spectroscopy, which is a multiple backscattering technique using a CCD camera to correlate the fluctuation of the backscattered light to the motion of the particles. By mathematical processing of the signal, the motion of the particles can be related to the viscoelastic properties of the sample, as particle speed and particle displacement are directly related to viscosity and elasticity. This work will give an overview of possible applications, with a focus on the Sol-Gel processes. Indeed, various functional and customized materials are prepared for a wide range of applications by the Sol-Gel process, and precise microrheological characterization could benefit to the optimization of preparation and properties of such materials properties. This work will show, how Rheolaser
have used the Q-tensor approach for nematic liquid crystalline systems and found conditions for formation of highly ordered phases where orientation order parameter approaches similar shape transformation was observed. Surprisingly the highly cross-linked hollow microgels under applying the uniaxial strain to the system could form liquid crystal phases. Uniaxial deformation of the simulation box with continuous microgels leads to reordering of the microgels. At the same time homogeneous deswelling, volume reduction and self-shape of the microgels is close to the Wigner-Seitz cell of the fcc-structure and two-fold compression still keeps the fcc ordering. Quite different behavior is observed for the case degree. Uniform compression of the simulation box with continuous microgels beyond the overlap regime leads to their compression with further shape transformation. Ultimate and hollow microgels (with cavity) subjected to uniform compression (concentration) and uniaxial deformations (one- or two-dimensional solvent evaporation). We have and deswelling mechanisms of microgels of different architectures and cross-linking density in overcrowded conditions. We propose computer simulations of regular (continuous) the soft particles upon concentration and crystallization? We can imagine that in addition to the spatial ordering, the shape and volume transformations of the microgels can occur transformations. It is well known that concentration of solid colloidal particles in suspensions can lead to their phase separation and/or crystallization. The latter means that the Polymeric microgels are soft colloidal particles highly sensitive to variation of environmental conditions (e.g. temperature, pH, etc.) leading to the volume and shape transformations. It is generally accepted that concentration of solid colloidal particles in suspensions can lead to their phase separation and/or crystallization. The latter means that the Polymeric microgels are soft colloidal particles highly sensitive to variation of environmental conditions (e.g. temperature, pH, etc.) leading to the volume and shape transformations. It is well-known that concentration of solid colloidal particles in suspensions can lead to their phase separation and/or crystallization. The latter means that the particles are spatially-ordered in the solution forming face-centered cubic (FCC) or hexagonal close-packed (HCP) structures. The natural question arises: What is going on with the soft particles upon concentration and crystallization? We can imagine that in addition to the spatial ordering, the shape and volume transformations of the microgels can occur upon concentration. In the current work we give a detailed description of the structure and dynamics of concentrated suspensions of soft microgels. We explore the deformation and deswelling mechanisms of microgels of different architectures and cross-linking density in overcrowded conditions. We propose computer simulations of regular (continuous) and hollow microgels (with cavity) subjected to uniform compression (concentration) and uniaxial deformations (one- or two-dimensional solvent evaporation). We have demonstrated that final structure of the microgels and their ordering strongly depends on the cross-linking density, relative size of the cavity (hollow microgels) and compression degree. Uniform compression of the simulation box with continuous microgels beyond the overlap regime leads to their compression with further shape transformation. Ultimate shape of the microgels is close to the Wigner-Seitz cell of the fcc-structure and two-fold compression keeps the fcc-structure ordering. Quite different behavior is observed for the case of the hollow microgels. The uniform compression leads to the spontaneous buckling of the microgels and cavity collapse. This is accompanied by breaking of the fcc-structure ordering. Uniaxial deformation of the simulation box with continuous microgels leads to reordering of the microgels. At the same time homogeneous deswelling, volume reduction and self-similar shape transformation was observed. Surprisingly the highly cross-linked hollow microgels under applying the uniaxial strain to the system could form liquid crystalline phases. Selected strain direction provides overall uniaxial deformation of the hollow microgels in such a way that they form disk-like objects which exhibit liquid crystalline behavior. We have used the Q-tensor approach for nematic liquid crystalline systems and found conditions for formation of highly ordered phases where orientation order parameter approaches
Increasing the particle density of a suspension of microgel colloids above the point of random-close packing, must involve deformations of the particle to accommodate the increase in volume fraction. By contrast to the isotropic osmotic deswelling of soft particles, the particle-particle contacts give rise to a non-homogeneous pressure, raising the question if these deformations occur through homogeneous deswelling or by the formation of facets. Here we aim to answer this question through a combination of imaging of individual microgels in dense packings and a simple model to describe the balance between shape versus volume changes. We find a transition from shape changes at low pressures to volume changes at high pressures, which can be explained qualitatively with our model. Whereas contact mechanics govern at low pressures giving rise to facets, osmotic effects govern at higher pressures, which leads to a more homogeneous deswelling. Our results show that both types of deformation play a large role in highly concentrated microgel suspensions and thus must be taken into account to arrive at an accurate description of the structure, dynamics and mechanics of concentrated suspensions of soft spheres.

References

SM06.03.03 Coarse-Grained Models for Predicting Microstructure of Crosslinked Gels

Eric Jankowski, Mike Henry, Carla E. Reynolds and Stephen Thomas; Materials Science and Engineering, Boise State University, Boise, Idaho, United States; The Boeing Company, St. Louis, Missouri, United States; The University of Tennessee.

Predicting gelation in polymer systems is difficult because of the long-time dynamics and complex components that characterize them. In this work we perform coarse-grained molecular dynamics simulations of reacting epoxies to access longer times and relevant volumes for observing up to 100nm features, gelation, and glass transitions. Here we focus on calculations that connect nanostructure to transition temperatures. We demonstrate that gelation and glass transitions depend on the degree of cure in epoxy systems, and quantify the degree to which coarse-grained models are predictive of experiments. We find that these coarse-grained models are quantitatively predictive of glass and gelation transitions for simple epoxy thermosets. Using GPU-accelerated simulations we demonstrate the potential for using coarse-grained models of polymer gels to provide a window into how processing protocols can be used to tailor the structure and properties of gels synthesized by crosslinking.

References
Magnetic microgels are colloidal particles consisting of a crosslinked polymer network with embedded magnetic particles [1,2]. The presence of magnetic particles inside the microgels is advantageous for many applications because in this case, magnetic microgels and their properties can be controlled by means of applied magnetic fields. However, magnetic microgels exhibit interesting behaviour even in the absence of an external magnetic field. In addition, the zero-field case provides a benchmark for understanding any changes in structural or magnetic properties when the field is applied. In this contribution, we focus on studying the properties of both single magnetic microgel particles and their suspensions by means of computer simulations in the zero-field case. We exploit our previously developed coarse-grained model for creating homogeneously and heterogeneously crosslinked microgels with a randomized internal architecture of the polymer network and incorporate ferromagnetic dipolar particles in a random manner [3]. Heterogeneous microgels have a distinct homogeneously crosslinked core and a shell. We examine microgels with different fractions of crosslinked monomers and content of magnetic particles in order to find out how these parameters influence the structural and magnetic properties of both homo- and heterogeneous magnetic microgels. Having the insight into single particle properties, we study microgel suspensions in order to understand what is the typical self-assembly scenario for magnetic microgels and how this scenario changes depending on magnetic content and density of the studied system.


SM06.03.05 Light and Temperature Dual Responsive Microgels Based on Spiropyran and N-Vinylcaprolactam Chaolei Hu1,2, Wenjing Xu1,2 and Andrij Pich1,2, Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany; 2DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany.

Light and temperature dual responsive microgels system based on spiropyran modified poly (N-vinylcaprolactam)-vinylamine copolymer was designed and built up. The novel and applicable microgels synthesis route involved first preparing spiropyran modified poly (N-vinylcaprolactam)-vinylamine copolymer via RAFT polymerization, hydrolysis and coupling, and then being crosslinked to microgels through W/O mini-emulsion. Light and temperature responsiveness of the synthesized microgels were investigated. The UV-vis spectrum demonstrated the reversible light-responsive behavior of microgels in aqueous solution, which comes from the spiropyran photosomerization under different irradiation. DLS results show that the microgels swell in darkness due to the-equilibrated gel particles feature spiropyran molecules in the polar, merocyanine form. After irradiation of visible light, the particle size becomes smaller because spiropyran changes to the relatively nonpolar, closed spiro form. DLS results also show the spiropyran modified microgels have temperature responsiveness: the microgels undergo a volume phase transition in water from a swollen state to a collapsed state with increasing temperature and the VPTT decreases corresponding the non spiropyran modified microgels due to the hydrophobic spiropyran units.

SM06.03.06 Fed-Batch, Temperature-Programmed Synthesis of µm-Sized Microgels—Closing the Size Gap Between Batch and Microfluidic Synthesis Agnieszka N. Ksiazkiewicz1,2, Wenjing Xu1,2 and Andrij Pich1,2, Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany; 2DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany.

Microgels or nanogels are cross-linked polymer networks that can respond to environmental change like temperature or pH. When triggered, they collapse or swell in solvents, while preserving their 3D structure. Micron-sized microgels can have plenty of interesting applications in crystallization studies, microlensing or mimicking cells. Microgels with the size above 10 µm can be synthesized using microfluidics [1]. However, very low yields and specific equipment requirements lead to high demand on synthesis of microgels via dispersion polymerization approaches. Moreover, the typical size of gels synthesized using standard batch polymerization reactions is in nanometer scale. Thus, particles ranging from 1 to 10 µm are hardly accessible, and means to obtain them need further investigation. Micron-sized poly(N-isopropylacrylamide) (pNIPAm) microgels have been obtained previously [2]; however, known toxicity and suspected cancerogenicity of pNIPAm disqualifies the usage of these gels in medical applications.

In contrast to pNIPAm, poly(N-Vinylcaprolactam) (pVCL) is non-toxic and biocompatible [3], making it a great candidate in medical and biomaterial fields. Here, for the first time, we have synthesized temperature-responsive pVCL microgels with large diameter (1-5 µm) via aqueous, surfactant-free precipitation polymerization. The size control was achieved by employing programmed temperature ramp during the nucleation stage of polymerization. In this work, the influence of various parameters such as monomer, cross-linker and initiator concentration, rate of temperature ramp, start and end temperature as well as dosing of the reagents was investigated. We were able to obtain microgels in different size ranges, depending on parameters altered.


SM06.03.07 Ultrahigh-Throughput Production of Monodisperse and Multifunctional Janus Microgels via In-Air Microfluidics Claas W. Visser, Ton Kamperman, Vasileios Trikalitis, Detlef Lohse and Marcel Karperien; University of Twente, Enschede, Netherlands.

Microfluidic chips can reproducibly generate large numbers of complex droplets and particles, but have a low throughput that blocks their industrial use. Furthermore, the resulting particles cannot be readily used as building blocks for solid (meta)materials, as they are contained by a liquid phase. Here we address these limitations by ejecting a train of droplets into the air and manipulating their properties by impact of a second liquid jet. The surface tension of the jet was reduced, so that it encapsulates the droplet by Marangoni spreading. Subsequent on-the-fly manipulations, including solidification and controlled deformation, enable fabrication of monodisperse emulsions, particles, and fibers with diameters of 20 to 300 µm at rates that are 10 to 100 times higher than usual microfluidic methods. Deposition of the partly-solidified droplets onto a solid substrate enables one-step manufacture of three-dimensional (3D) multiscale materials. For example, we demonstrate an artificial pancreatic tissue in which each solidified droplet forms a controlled micro-environment for MN6-cells that maintain their capacity to proliferate and produce insulin. In-air microfluidics, as we name this approach, enables fabrication of controlled multi-material particles and capsules at industrially relevant rates (up to 3 ml/minute/ nozzle). I will present recent results including the fabrication of multifunctional Janus particles for enzymatic cascade reactions, and sketch how In-air microfluidics may contribute to one-step fabrication of multi-scale materials with controlled mechanical, biological, or thermal properties.
rigid nanoparticles, flexible macromolecules, micelles or vesicles. When swollen, they are soft and have a fuzzy surface with dangling chains and the presence of cross-links provides structural integrity - in contrast to linear and (hyper-) branched polymers. Finally, microgels reveal interface activity without being amphiphilic. Due their properties, microgels can be used to tune the colloid-to-polymer transition.

We will discuss properties of microgels of different architecture (e.g. ultra-low crosslinked, hollow, multi-shell) both in aqueous solution and at interfaces. These microgels respond to various stimuli as, e.g. temperature and pH, and enable uptake and release applications. The structure of microgels and complexes with guest species are investigated by means of scattering methods, especially exploiting the technique of contrast variation in small angle neutron scattering. The experimental results are be compared to computer simulations. In addition, superresolved fluorescence microscopy is employed.

Microgel adsorb to fluid and rigid interfaces surfaces and their response to external stimuli allows preparing responsive emulsions and coatings which can be used in biocatalysis and as sensors. Interfaceal properties are probed via compression isotherms as well as by scanning force and fluorescence microscopy.


9:00 AM *SM06.04.02 Dynamics of PNIPAM Microgels at Liquid Interfaces Valérie Ravaine1, Véronique Schmitt2, Joris Sprakel1, Louis Keal3 and Cecile Monteux4; 1ENSCPB, Bordeaux, France; 2Wageningen University, Wageningen, Netherlands; 3CRPP, Bordeaux, France; 4ESPCI, Paris, France.

We investigate the drainage dynamics of thin liquid foam films containing PNIPAM microgels suspensions with two cross-linking densities (1.5 % or 5% mol BIS) and at two microgel concentrations (0.1 and 1% wt). For this purpose we use a thin film pressure balance apparatus that can apply a controlled and sudden hydrostatic pressure on the film and record the subsequent film thinning as a function of time. Once the film thickness has reached a stationary value, we test the adhesion between the interfaces of the film by reducing the pressure and measuring the angle between the film and the meniscus. This angle increases on reduction of pressure for adhesive films, which resist the separation of their interfaces. Non-adhesive films separate easily, and the meniscus angle stays constant. At low microgel concentration, the more densely cross-linked microgels (5% mol BIS) tend to drain into more adhesive films than the more loosely cross-linked particles (1.5% mol BIS). The adhesion results from particles that bridges the two air-water interfaces constituting the film, i.e. particles being shared between both interfaces of the films. In those cases, the film, which is initially stabilized by a bilayer of microgel particles rearrange to a state where the particles are shared by them. These results are discussed and compared with previous studies at low concentration of microgels, which have shown that emulsions stabilized with densely crosslinked microgels are more adhesive and less resistant to mechanical stresses than those obtained with lower cross-linking densities. In addition micron-scale depleted zones with no microgels are observed in the films stabilized with the 5% mol BIS particles, which eventually lead to the rupture of the film. At 1% wt, the films drain slowly, are not adhesive and have the thickness of a bilayer of microgels while at 0.1% wt, the films have the thickness of a monolayer of microgels, are adhesive and show bridging. From the thin liquid foam film thicknesses we extract a rough estimation of the radii of adsorbed particles in the thick-films before applying the pressure. Our results are consistent with particles being adsorbed in a spread conformation for the 0.1% wt sample and in a compressed conformation for the 1% wt sample. In line with previous studies on emulsions, we conclude that a larger surface coverage may reduce rearrangements, thus preventing bridging.

9:30 AM SM06.04.03 Microgels at Liquid-Liquid Interfaces—Comparing Experiments with a Realistic Model Fabrizio Camerin1,2; 1Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Sapienza University of Rome, Roma, Italy; 2Institute for Complex Systems, National Research Council, Roma, Italy.

A distinctive feature of microgel particles is that of being soft colloids with an internal polymeric architecture. At liquid interfaces, in particular, they deform and flatten significantly due to the balance between surface activity and internal elasticity. For this reason, recent experimental studies have shown that they are a valuable choice to stabilize smart emulsions in contrast to common rigid colloids [1, 2]. Despite the clear potential this system could bring, a detailed theoretical understanding of the phenomenon is still lacking. In fact, commonly accepted models in which the internal structure is neglected or diamond-like, where polymer chains have a fixed length, are not able to reproduce this behavior, especially by the fact that the corona would not flatten out. Conversely, we have now provided a realistic model that reproduces in silico the polymeric network of PNIPAM microgels [3], even in the presence of an explicit solvent [4].

By placing the microgel at liquid-liquid interfaces, we can now directly compare the morphology of the microgels resulting from simulations with in-situ cryo-electron microscopy measurements and AFM imaging after Langmuir-Blodgett depositions [5]. The correct modelling of the internal degrees of freedom allows for a qualitative comparison with the experimental outcomes and to report a consistent trend as a function of the fraction of crosslinkers. By varying the parameters of the monomer-solvent potential, we are able to selectively tune the surface tension, as expected for different combinations of solvent at the interface. This opens up the possibility to evaluate single-particle elastic properties and effective interactions among microgels, that can be used to predict macroscopic behavior. These are also essential to develop predictive power for the use of microgels in a broad range of applications.


9:45 AM BREAK

SESSION SM06.05: Rheology and Nanomechanics of Microgels II

Session Chairs: Christos Likos and Igor Potemkin

Wednesday Morning, April 24, 2019

PCC North, 200 Level, Room 228 A

10:15 AM *SM06.05.01 Microgel Morphology Resolved by Mesoscale Computer Simulations Roland G. Winkler; Theoretical Soft Matter and Biophysics, Institute for Advanced Simulation, Forschungszentrum Juelich GmbH, Juelich, Germany.

The structural properties of microgels adapt to external stimuli by swelling or shrinking in response to changes in temperature, pH, ionic strength of the solution, or solvent composition [1]. This renders them ideal candidates for a broad range of applications including encapsulation for drug delivery, sensing, and food additives. The possibility to change the microgel composition during the synthesis opens an avenue for novel applications. An example is the synthesis of core–shell microgels, which are typically comprised of polymers with distinctly different properties, e.g., their hydrophobicity, which allows for the control of the microgel morphology, and opens an avenue for novel applications [2].
Here, we present results of hybrid simulations combining the multiparticle collision dynamics method [3] for the fluid with molecular dynamics simulations for the microgel to systematically characterize the morphologies of core–shell microgels [2]. With increasing hydrophobic interaction of the shell polymers, we observe drastic morphological changes of the microgel from a core-shell structure to an inverted microgel, where the core is turned to the outside, or a microgel with a patchy surface of core polymers directly exposed to the environment. A phase diagram is established of the various morphologies.

Moreover, the morphologies of a microgel are analyzed during collapse from a swollen soft, deformable networks with a fuzzy surface to a colloid with homogeneous density and a sharp surface, which is achieved by solvent exchange [1]. Time-resolved small-angle x-ray scattering experiments and computer simulations unambiguously reveal a two-stage process: In a first, very fast process, collapsed clusters form at the periphery, leading to an intermediate, hollowish core-shell structure that slowly transforms to a globule. This structural evolution is independent of the type of stimulus and thus applies to instantaneous transitions as in a temperature jump or to slower stimuli that rely on the uptake of active molecules from and/or exchange with the environment. The fast transitions of size and shape provide unique opportunities for various applications as, for example, in uptake and release, catalysis, or sensing.

template. As the hydrogel is a water-swollen network of hydrophilic polymers, the microgel matrix is highly permeable to small molecules while being impermeable to the macromolecules larger than its limiting mesh size. Moreover, as the average mesh size is controllable by adjusting the molecular weight of gel-forming monomers, the cut-off threshold of permeation is tunable. Taking advantages of the hydrogel for SERS analysis, we microfluidically prepare monodisperse microgels containing metal nanoparticles. The microgels exclude adhesive macromolecules while allowing infusion of small target molecules to the surface of metal nanoparticles. Therefore, Raman intensity for the target is tunable. Taking advantages of the hydrogel for SERS analysis, we microfluidically prepare monodisperse microgels containing metal nanoparticles. The microgels exclude adhesive macromolecules while allowing infusion of small target molecules to the surface of metal nanoparticles.
characterized by high network inhomogeneity due to polymer chain bundling, which accelerates the network collapse. We probe the effect of crosslink density on the volume transition and show that its decrease leads to a sharper volume phase transition near the critical point. Finally, we examine the bulk modulus of compressed microgel suspensions at different packing fractions and solvent conditions. We evaluate the degree of particle-particle penetration to establish its relation to the micromechanics of compressed microgel suspensions.

4:30 PM SM06.07.03Towards High Throughput Microfluidic Devices Alexander Jans and Alexander J. Kuehne; DWI-Leibniz Institute for Interactive Materials, Aachen, Germany.

Droplet based microfluidic is a versatile tool to generate confined volumes in form of an emulsion. In contrast to bulk emulsification techniques, microfluidics produces highly uniform droplets, which act as templates for chemical reactions. Microfluidic emulsification has been used in particular to create functional and soft colloidal structures. In the microfluidic drop-maker, these particles are generated consecutively one-after-the-other and the yield over time is low with a single drop-maker.

To overcome this challenge, several approaches were taken by parallelizing in ladder- or tree- type structures using PDMS based systems and soft-lithography, resulting in large footprint devices with large dead volumes. We could show that by producing microfluidic devices by rapid prototyping we can stack drop-makers on top of each other and minimize the device footprint and overall channel length. Furthermore, such 3D printed microfluidic devices enable new design strategies, which are impossible to obtain using common soft-lithographic approaches. To showcase the freedom of design in 3D prototyped devices we designed a helical channel structure device where all drop-makers disperse into a single continuous channel. This design leads to significantly increased droplet concentrations of the dispersed phase. Compared to individual drop-makers the volume fraction of droplets is up to 300% higher. Double emulsions have also received a high interest in biomedical applications because of their potential to produce monodisperse capsules and facile loading protocols with diameters on the micrometer scale. Classical (glass capillary and PDMS) devices lack durability and required surface modification while parallelization strategies remain complicated. We present a new system based on a 3D printed device that utilizes the advantages of rapid prototyping to produce double emulsions in three or more parallelized channel geometries for high throughput reaction containers for polymer and microgel capsules.

References

4:45 PM SM06.07.04Strategies to Realize Precise Macroscopic Supramolecular Assembly Mengjiao Cheng; Beijing University of Chemical Technology, Beijing, China.

Macroscopic supramolecular assembly (MSA) investigates multivalent interactions between building blocks larger than 10 micrometer and modified with numerous interactive motifs. MSA has provided a platform for fundamental understanding of various interfacial phenomena such as underwater adhesion, self-healing etc. Because large interactive interfaces of macroscopic building blocks have induced more kinetic possibilities, the assembled structures are normally poorly-ordered, which is not favorable for practical applications. To address the problem of macroscopic self-assembly processes being insensitive to errors and having poorly aligned assemblies, we have proposed two strategies for precise self-assembly by (1) pre-orientation of building blocks or (2) post-method of self-correction. The first strategy applies long ranged forces (capillary forces, magnetic forces) by anisotropic surface modification of the building blocks and may ameliorate the precision to some degree. However, the essence of insensitivity to errors still leads to some defects. Therefore, we used the second strategy of self-correction to realize precise MSA: through suitable control over the disassembly kinetics, the poorly and precisely aligned structures could be self-identified and selectively disassembled the poorly aligned structures, which led to re-assembly of the building blocks; after cyclic iteration of disassembly and re-assembly, we could achieve precise MSA of all interactive pairs.

References
we demonstrate a number of new effects. The microgels can serve as compatibilizers of immiscible molecules.\textsuperscript{1,2} In particular, we demonstrate that two initially immiscible liquids, A and B (oil and water), can partially or fully be mixed within the microgel adsorbed at their interface. If the incompatibility of the liquids is relatively low, they form a homogeneous mixture outside the whole microgel particle being segregated outside. As the incompatibility grows, separation into two (micro)phases within the microgel occurs. We demonstrate this effect for homopolymer\textsuperscript{1,2} and amphiphilic\textsuperscript{1} (AB-copolymer) microgels.

Adsorption of the microgels on a solid surface leads to their flattening: the shape of the microgel is determined by a balance between the gain in the energy of adsorbed monomer units and the penalty in the elastic free energy of the subchains subjected to lateral stretching. Despite a strong interaction with the surface, the adsorbed microgels are able to swell and collapse in response to environmental changes (pH and temperature) varying the size on the surface. We have demonstrated a peculiar behavior of the microgels adsorbed on a patterned surface (planar surface with cylindrical holes or pores).\textsuperscript{4} It turns out that a microgel can enter and exit a narrow cylindrical pore under external stimuli leading to collapse and swelling of the microgel. Attractive interactions between the microgel and the pore surface stimulate the microgel entering upon its collapse. The entering is driven by a gain in the surface energy: the area of the microgel-pore contacts is maximized within the pore. Swelling of the microgel within the pore of a finite size is thermodynamically favorable if the pore thickness exceeds a certain threshold value. Otherwise, the swelling leads to the microgel exit. The physical reason for this is a gain in the elastic free energy of the subchains which are less stretched outside the pore. We systematically study swelling and collapse of the microgel within the pore. Both longitudinal size and radial concentration profiles are calculated for different strength of the beads with each other and the pore surface. We predict an intra-microgel “phase” coexistence leading to the formation of a dense adsorbed layer near the pore surface and highly swollen central part of the microgel. Furthermore, the permeation of nanoparticles, whose size is smaller than the mesh-size of the microgels was simulated under different swelling and adsorption degrees. It is demonstrated that the microgel can slow down and completely stop the permeation of nanoparticles through the pore.

Acknowledgement. Financial support of the Russian Science Foundation, project # 15-13-00124 is gratefully acknowledged.

References:


9:30 AM SM06.08.03

Pickering Emulsions Stabilized by Microgels—Link Between Microgel Adsorption at Model Interfaces and Emulsion Properties Marie-Charlotte Tatry\textsuperscript{1, 2, 3}, Véronique Schmitt\textsuperscript{1} and Valérie Ravaïne\textsuperscript{1, 2, 3};\textsuperscript{1} Centre de Recherche Paul Pascal, Centre National de la Recherche Scientifique, PESSAC, France;\textsuperscript{2} Institut des Sciences Moléculaires (Nysa), Centre National de la Recherche Scientifique, PESSAC, France;\textsuperscript{3} University of Bordeaux, PESSAC, France.

Microgels are soft and deformable colloidal particles which can be swollen by a solvent and adsorbed at liquid interfaces. The well-known poly(N-isopropylacrylamide) (pNIPAM) microgels are thermo-sensitive and exhibit a volume contraction when the temperature is raised above the volume phase transition temperature (VPTT). These particles have shown high potential as Pickering emulsions stabilizers: emulsions could be stable at temperatures below the VPTT and be destabilized on-demand above it \cite{1}. Understanding microgel adsorption at model interfaces gives better insight into the link between microgels conformation, mechanical properties of the interface and properties of the resulting emulsions \cite{2, 3}.

In this work, we highlight the role of structural parameters such as the cross-linking density i.e. the microgel deformability, their size or the presence of charges through the use of pH sensitive groups or in-situ (pH, electrolyte concentrations). For that, a systematic approach is adopted using two complementary methods: the spontaneous adsorption and the forced compression. Both equilibrium and kinetics studies are conducted: by the pendant drop method, we examine the microgel interfacial properties, measuring the dynamic surface pressure, tension and the dilational visco-elasticity \cite{4}. By the Langmuir film technique, the conformations and packing of microgels as a function of surface pressure could be discussed \cite{3}.

Moreover, microgels deformation and adsorption at the liquid interface have consequences on emulsion macroscopic properties (stability, flocculation, etc.). Despite the complexity of comparison, spontaneous adsorption of microgels at model interfaces can be correlated with the microgels conformation in emulsions or foam films in which microgels are locked into various conformations and with the emulsions properties. Taking into account the kinetics of adsorption at the interface and processing conditions, we could control emulsification pathways from high energy methods to microfluidics.

Finally, on the basis of this knowledge, we show how the concept can be extended to new designed microgels that are responsive to other (bio)-stimuli such as glucose \cite{5}.


\textsuperscript{4} Tatry et al., in preparation.

\textsuperscript{5} Tatry et al., in preparation.

9:45 AM BREAK

SESSION SM06.09: Interactive Microgels and their Assembly II

Session Chairs: Yu Hoshino and Regine von Klitzing

Thursday Morning, April 25, 2019

PCC North, 200 Level, Room 228 A

10:15 AM SM06.09.01

Macroscopic Supramolecular Assembly and Its Applications Feng Shi; College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing, China.

Macroscopic supramolecular assembly (MSA) is a recent progress in supramolecular chemistry regarding assembly events between building blocks larger than ten micrometer. Researches on this topic have provided both a deep fundamental understanding of interface-interface molecular recognition in a multivalent manner and a novel methodology for the fabrication of supramolecular materials. To address the problems of “what kind of building blocks could achieve macroscopic assembly?”, we have established a general design rule of MSA that assembly probability decreases with the increasing elastic modulus of building blocks. Moreover, we have proposed the concept of “flexible spacing coating” to achieve MSA of rigid materials. To promote the practical applications of MSA, we have fabricated biocompatible 3D structures with targeted chemical modification, which provide a novel strategy to address the current challenges in fabricating complex 3D tissue scaffolds with localized protein for further cell differentiation.

10:45 AM SM06.09.02

Simulating the Response of Liquid Crystalline Elastomer Microposts to Light James T. Waters\textsuperscript{1}, Joanna Aizenberg\textsuperscript{2} and Anna Balazs\textsuperscript{1};\textsuperscript{1} University of Pittsburgh, Pittsburgh, Pennsylvania, United States;\textsuperscript{2} Harvard University, Cambridge, Massachusetts, United States.

Liquid crystalline elastomers (LCEs) represent a realizable physical system that can exhibit a large, non-linear response to an environmental stimulus. By adding light-sensitive
moieties to the mesogens responsible for liquid crystalline order, one can create elastomers that will change shape in response to ultraviolet light. This provides a basis for a “write once, read many times” (WORM) memory. Information is encoded in an array of LCE microposts through a magnetic field during cross-linking, and then read out by introducing a light source. The system will return to its initial state upon removal of the stimulus, allowing the reading process to be repeated without altering the system. We developed a finite element simulation code to study components of such a system. Using our simulation method, we can predict the micropost deflection as a function of the preset nematic director and the incident angle of the light. We make comparisons to available experimental results and describe new findings that reveal how light can be used to regulate the structure of an array of multiple, interacting LCE microposts. These studies point to new ways of utilizing the LCE arrays for technological applications.

11:15 AM SM06.09.03
2D Binary Microgel Alloys for Soft Nanotemplating Miguel Angel Fernandez Rodriguez, Maria-Nefeli Antonopoulou, Fabio Grillo, Dominic Gerber and Lucio Isa; Interfaces, Soft Matter and Assembly, Department of Materials, ETH-Zurich, Zurich, Switzerland.

2D binary colloidal alloys are useful structures as colloidal models and for nanofabrication applications. Up to now, only close-packed binary colloidal assemblies on a substrate have been reported. We instead report a versatile sequential deposition method using differently sized PNIPAM based microgels. We are able to produce complex assemblies with decoupled density gradients for the two particles and with fine control over the interparticle distance. The delicate interplay between capillary attraction and steric repulsion at an oil-water interface allows obtaining a broad range of crystalline microstructures. After deposition on a silicon wafer, such assemblies can be further used as masks for wet etching to obtain Vertically Aligned Nanowires (VA-NWs) with applications in photonics, cell transfection or superhydrophobic surfaces. We synthesized microgels and used a Langmuir trough to deposit the microgels from the water/hexane interface onto silicon substrates. In order to get the binary assemblies, sequential depositions of the microgels of different sizes were performed. This protocol allows the independent control of the interparticle distance for each particle type, e.g. achieving a gradient of interparticle distance for the small microgels while the big microgels are kept at a fixed interparticle distance. Moreover, through the fine-tuning on the microgel architecture and of the deposition parameters, square lattices can be obtained thanks to a fine balance between capillary quadrupolar attraction and steric repulsion at the water/hexane interface. AFM images were taken to characterize the transferred assemblies and HF wet etching enabled producing VA-NWs using the binary colloidal assembly as masks for metal-assisted chemical etching. Such VA-NWs have interesting optical properties, ranging from iridescence to structured colors and wavelength modulation, depending on the geometry of the VA-NWs, which we characterized with reflectivity measurements and compared to simulations.

11:30 AM SM06.09.04
Field-Induced Reconfigurable Assembly of Spherical Ionic Microgels into Crystals and Microtubules Brittita Joseph Bonifaç1, 2 and Peter Schurtenberger1; Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden; 2Centre for Nanoscience and Nanotechnology, Sathyabama Institute of Science and Technology, Chennai, India.

Electric field induced assembly or field-directed self-assembly is a very attractive path towards the creation of 3D ordered structures. Previous experiments with soft ionic microgels (5 mol% cross-link density) have indeed revealed the existence of different fluid and ordered and amorphous solid phases as a function of effective volume fraction and field strength [1]. Moreover, they provided evidence for a novel field-induced phase transition scenario with multiple path-dependent routes for phase-transition kinetics, and the existence of long lived metastable crystal states that were thought to be due to the ability of these particles to partially interpenetrate and form long-lived entangled states [1,2]. Here we now use ionic microgels in order to investigate the importance of particle softness on the resulting field-induced state diagram. The ionic microgels used in the study are made up of poly(N-isopropylacrylamide)-co-acrylic acid (PNIPAM-co-AAc). The more densely crosslinked particles (10 mol%) at low particle concentrations and at low field strengths (at 0.5 and 0.6kV/cm) form a fluid string phase. As the field strength is further increased, the particles assemble into islands of small body-centered tetragonal (BCT) crystals co-existing with a gas phase. These results are consistent with the field measurements on moderately crosslinked microgels [1,2]. At higher field strengths however, the BCT sheets fold and adopt a regular tubular structure reminiscent of a single-walled microtubule. The tubular assembly can be reconfigured by switching ON/OFF the field. While ellipsoidal particles (polystyrene core, PNIPAM-co-AAc shell) polarized in an external electric field were observed to associate into well-defined tubular structures [4], no comparable self-assembly processes have been reported for hard or soft spherical particles so far. Here we present a systematic study of the field-induced self-assembly of ionic microgels as a function of crosslink density, particle concentration, field strength, and discuss the underlying phase transition kinetics and pathways for the various liquid-solid and solid-solid transitions present.

References

11:45 AM SM06.09.05
Soft Material Programming Through the Spatiotemporal Release of Oligonucleotides Moshe Rubanov, Phillip J. Dorsey, Dominic Scalise, Wenyu Wang and Rebecca Schulman; Johns Hopkins University, Baltimore, Maryland, United States.

The programmable spatiotemporal release of molecular outputs is a prerequisite for creating new classes of stimuli responsive biomaterials capable of executing sensing and computational programs. Here we demonstrate the ability to fabricate heterogeneous micromaterials that implement sequentially activated molecular cascades with programmed timescales of activation and release from a hydrogel. These materials use DNA-based strand-displacement to direct the sequential release of short oligonucleotides from spatial domains. Maskless photolithography enables the spatial sequestration of acrylate-modified short oligonucleotides for local hybridization reactions within hydrogels at sizes of tens of microns. To control temporal release, we used a toehold mediated DNA strand displacement reaction cascade that allows for the controlled release of oligonucleotides at 8-hour intervals. This system could be used to direct chemo-mechanical actuation within soft-robots or as a local chemical clock to sequentially coordinate movement. The programmed release of DNA oligonucleotides from hydrogel substrates enables the scalable development of DNA-based reaction-diffusion systems that regulate the availability of oligonucleotides at different points in space and time.

SESSION SM06.10: Towards New Applications of Colloidal Gels II
Session Chairs: Michel Cloitre and Shin-Hyun Kim
Thursday Afternoon, April 25, 2019
PCC North, 200 Level, Room 228 A

1:30 PM *SM06.10.01
Why Microgels are Ideally Suited to Improve the Performance of Next Generation Solar Cells Brian Saunders; School of Materials, University of Manchester, Manchester, United Kingdom.

Microgels are well-known swellable colloidal gel particles that have been studied for more than 80 years. They have excellent colloidal stability in their swollen (micрогel) state due to their inherently low effective Hamaker constant and this is augmented by steric and electrostatic repulsion. Microgels also have excellent synthetic versatility which enables water- or organic-swelling microgels to be synthesised in a scalable manner (to the multi-tonne scale). In less than a decade the power conversion efficiency of solution processable perovskite solar cells (PSCs) has, remarkably, increased from a few percent to greater than 23%. This incredible rate of efficiency increase is unprecedented in the history of solar cell research. PSCs are remarkably tolerant to additives and are scalable to, potentially, multi-megawatt deployment scale at low cost. In this discussion an overview of our recent work using microgels as additives to improve the performance of PSCs is discussed. Polystyrene microgels enable lower concentrations of expensive conjugated polymers to be used for the hole-transport matrix part of PSCs and also improve the stability[1]. Poly[N-vinylformamide] microgels enable micropatterning of the perovskite capping layer of PSCs to produce an unexpected disordered inverse opal morphology which improved the efficiency compared to control devices[2]. Recent results obtained using microgels in other parts of the solar cells to enhance PSC performance will also be presented. Because microgels and PSC technologies can be combined in a variety of ways to give performance benefits and both are potentially low cost this hybridisation of old and new technologies has a bright future.
Stable, inexpensive and high-performance CO2 separation membranes are of significant interest as a key materials to sequester CO2 from exhaust gases of fire plants. In order to achieve the membranes procedure to create defectless CO2 permeable membranes which thickness is smaller than micrometer scale have to be developed. We have reported that temperature responsive hydrogel-particles containing amine groups can reversibly absorb large amount of CO2 in response to the temperature dependent phase transition of hydrogels (JACS, 134, 18177, 2012. Angew. Chem. 53, 2654, 2014). In this presentation, we report that ultrathin hydrogel membranes of thickness below 100 nm can easily be prepared by deposition of the microgel particles on the top of porous films. The membranes showed CO2 selective permeability against nonacidic gases such as N2.

References:

SYMPOSIUM SM07

Bioinspired Materials—From Basic Discovery to Biomimicry
April 23 - April 25, 2019

Symposium Organizers
Aránzazu del Campo, INM-Leibniz Institute for New Materials
Matthew Harrington, McGill University
Niels Holten-Andersen, Massachusetts Institute of Technology
Ali Miserez, Nanyang Technological University
Mussel Adhesion Needs a Battery

Herbert Waite; MRL, University of California, Santa Barbara, Santa Barbara, California, United States.

The wet adhesion of mussels, although incompletely understood, has inspired numerous translational studies seeking to capture its strength, toughness and versatility. Given the Dopa-rich interfacial proteins in mussel adhesion, most translations depend on adopting Dopa or catechol functionalities for a variety of synthetic backbone chemistries. Although notable short-term successes have been reported, a robust and durable adhesive formulation based on catechol or Dopa has yet to emerge. The reason for this is fairly obvious: catechols including Dopa are prone to oxidation. Although oxidation products such as quinones have some use in promoting cohesion as cross-linking agents, they have poor adhesion on most surfaces. Despite the very oxidizing influence of seawater, catechol-mediated mussel adhesion does not succumb to this limitation. Indeed, adhesive plaque interfaces remain reducing after months of service in the sea. Current evidence supports that mfp-5 with >25 mole % Dopa deposited as a 10-20 nm thick film is the functional adhesive bound to surfaces by its Dopa and lysine functionalities. On top of this, sits an mfp-3 rich hydrogel about 100-200 nm deep. Mass spectrometry reveals that the Dopa in mfp-3 remains intact despite the ambient oxidizing environment. As mfp-3 variants coacervate during deposition there is conjecture that coacervates are insulating Dopa but the mechanism for this is not yet understood. Certainly, mfp-3 in aqueous solution at pH8 undergoes spontaneous oxidation. Segregation of different redox-active proteins into specific compartments resembles a battery. The mfp-5 containing adhesive film is one compartment; mfp-3 and mfp-6-containing coacervate droplets is another. These two share a common but immiscible interface for redox exchange. Assuming that the film of mfp-5 is vulnerable to oxidative damage and given that mfp-3/6 within coacervate droplets is shielded from oxidation, the reservoir of reduced mfp-3 should offer electrons and protons to restore damaged Dopa in mfp-5 until mfp-3 and -6 are depleted. The significance of this to translational studies is clear: if the aim is to make synthetic adhesives based on Dopa, then the adhesive has to be engineered to include a redox reservoir or battery that will maintain the surface-bound catechols against oxidative damage.

Bio-Inspired Programmable Surfaces for Switchable Wetting and Adhesion

Kurtis A. Laqua and Benjamin D. Hatton; University of Toronto, Toronto, Ontario, Canada.

The microstructures of natural surfaces, such as plant leaves, reptile skin and ciliated tissues can be actuated to provide dynamic, adaptive properties of wetting, transport, and adhesion [1]. Examples include the gecko and the octopus, which can reversibly switch their adhesion to a wide variety of opposing surfaces. Yet, most synthetic surface structures are static, lacking an ability to change dynamically in response to their environment or an applied signal. This work explores how adhesion, friction, and wetting can all be controlled through bio-inspired dynamic surfaces. By engineering the shape, scale, and spacing of surface microtopography on silicone layers, interfacial contact and interaction can be modified. Our dynamic microtopography devices will show droplet wetting transition from Cassie-Baxter to Wenzel, switchable adhesion to structured or flat surfaces and tunable friction capable of ~50% change in peak frictional force. [1] Gorb S. Functional surfaces in biology: mechanisms and applications. CRC Press; 2006. p. 381-97.

Sticking Like Barnacles—Unraveling and Mimicking a Natural Adhesive

Christopher So1, Kenan Fears1, Elizabeth Yates2, Luis Estrella1 and Kathryn Wahl1; 1Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; 2Chemistry, U.S. Naval Academy, Washington, District of Columbia, United States.

Macro fouling organisms have plagued mariners and scientists alike since the sailing of the first ships in the ocean. Even today, combating fouling is a global challenge with great economic burden on the world’s navies and maritime operations. Over the last year, our team has applied modern bioinformatic approaches to produce a new, more comprehensive picture of the specialized proteins found in the adhesive of one of the most tenacious fouling organisms in the ocean: the acorn barnacle. Barnacles produce a micron-thick layer of ordered amyloid-like nanofibers from proteins that function as a permanent wet adhesive. Recent proteomic sequencing of the dissolved barnacle glue reveals that, like other fibrous biomaterials such as silk and elastin, small and flexible amino acids play a key role in forming the mesh-like adhesive. Their well-defined, modular, nature result in novel biomaterials that serve many purposes: adhesion, durability, bacterial resistance, and even potent enzymatic activity. Fibers are shaped by a highly conserved domain alternating between short 20-residue low complexity sequences (Gly/Ser/Thr/Ala residues) and regions with alternating charged and non-charged side chains, with more than 80 such domains in just five proteins. The adhesive properties of these unique sequences and their function in an amyloid-like structure remain unclear.

To develop the sequence basis of cement formation, we design short synthetic peptides from homologous cement proteins. Short synthetic peptides demonstrate that materials are formed through a set of patterned sequences that exert specific control over polymerization, curing, and adhesion using recognition mechanisms similar to how globular proteins recognize each other, i.e., structure-based recognition. Specifically, we find that patterned charge domains recognize and activate otherwise dormant peptide sequences through recognition of a unique anti-parallel beta sheet structure as measured by FTIR. While charged domains favor an anti-parallel structure, sequences without charged domains switch fibril assembly to parallel beta sheet aggregates. Our work demonstrates that the structures produced by patterned cement sequences, and the progression of domain interactions, are critical in polymerizing materials that resemble the natural adhesive. Finally, to understand whole protein self-assembly, we demonstrate that emergent platforms such as engineered bacterial biofilms are a viable route for the growth of recombinant cement materials as well as for mapping protein and peptide interactions. Synthetic and recombinant adhesive materials provide a route to scale up and study a scarce but potent class of multifunctional adhesive nanostructures produced by one of the oldest adversaries of naval and maritime technologies.

Functional Superhydrophobic and Icophobic Coatings Made of New Biomimetic “Gecko Leg” Soft dendritic Colloids

Austin Williams, Sangchul Roh and Orlin Velev; Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States.

We will report how coatings and nonwovens with outstanding superhydrophobic and icophobic properties can be made from novel types of polymer particles with controlled morphologies and interactions. First, we will introduce the synthesis of a new class of particles named soft dendritic colloids (SDCs). These particles are hierarchically structured, with a branched corona of nanofibers spreading out in all directions. They are nanomanufactured by multiphasic polymer precipitation under intensive shear. The nanofiber corona around these “gecko leg” particles endows them with extraordinary strong adhesion to almost any surface and to each other, and enables unique structure-forming abilities. These particles exhibit the phenomenon of “contact splitting”, which is displayed in the remarkable adhesion of gecko feet. The morphological similarity of the SDCs to the gecko lizards’ setae endows the SDCs with excellent dry adhesion and cohesion properties. The hierarchical surface roughness resulting from the overlapping SDC micro- and nanofibers allows the facile formation of superhydrophobic and superhydrophilic coatings depending on the properties of the polymer used. The adhesion of SDC coatings to substrates can be further improved both through the addition of a poly(dimethyl) siloxane (PDMS) binder and by creating bicontinuous networks of SDCs composed of different polymers. The addition of a PDMS binder and formation of bicontinuous SDCs network modify the surface roughness and contact angle of the SDC coatings and lead to improvements in durability, wettability, and anti-icing properties, including increased ice nucleation time and decreased ice adhesion strength when compared to uncoated and SDC coated substrates. The new functional coatings can find applications in numerous industrial and consumer products.

Morphological Examination of the Adhesive Setae Across the Toepads of Anolis Lizards—Insights into the Fundamentals of Fibrillar Adhesives

Michael C. Wilson1, Austin Garner1, Anthony Russell2, Peter Niewiarowski2 and Ali Dhimojwala1; 1University of Akron, Akron, Ohio, United States; 2University of Calgary, Calgary, Alberta, Canada.

Gecko-inspired fibrillar adhesives have become increasingly prevalent over the past two decades because of the multifunctional behavior exhibited in gecko adhesive toepads,
including self-cleaning, controlled releasability, and reversibility. Many challenges remain in replicating this multifunctionality, a major one being understanding the role of the complex morphology: microscopic hierarchy of the adhesive setae and their macroscopic patterning across the toepad. Deconvolution of the structural effects in producing the desired properties remains daunting, because setal structure is very complex. However, fibrillar adhesion has been independently evolved by Anolis lizards, and these lack the hierarchical branching of their setae. Thus, anole setae more closely resemble the theoretical models used to explore the principles of fibrillar adhesion and the synthetic seta-like fibrils that have been employed in the generation of synthetic adhesives. In this study, we employ scanning electron microscopy to examine the setal dimensions and patterning of Anolis lizards across the toepad and compare our findings with the attributes of the fibrillar adhesives of geckos. Detailed morphological characterization of Anolis adhesive setae provides information which can be used to understand the potential emergent properties of hierarchical complexity and patterning of lizard fibrillar adhesives.

SESSION SM07.02: Bioinspired Materials—From Basic Discovery to Biomimicry II

Tuesday, April 23, 2019
PCC North, 200 Level, Room 226 C

1:30 PM *SM07.02.01  
Bioinspired Elastin-Based Adhesives  

Julie C. Liu; Purdue University, West Lafayette, Indiana, United States.

A successful biocompatible adhesive must be biocompatible, set in a wet environment, match the mechanical properties of the surrounding tissue, and have proper adhesive and cohesive properties. Current technologies do not meet these needs. We developed bioinspired protein-based adhesives that combine adhesion from DOPA residues found in mussel adhesive proteins with the mechanical properties of elastin, which can also coacervate in response to the environment. We demonstrated that these proteins are cytocompatible, provide the strongest bonds of any rationally designed protein when used completely underwater, and can be easily applied underwater because they coacervate in physiological conditions. Recently, we investigated different formulations in physiologically relevant environments by using pig skin substrates and curing in a warm, humid environment.

2:00 PM SM07.02.02  
Extremely Tough Cyclic Peptide Nanopolymers  

Manoj K. Kolel-Veetil, Luis Estrella, Christopher So and Kenan Fears; Chemistry Division, U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

We present a new class of bioinspired nanomaterials that are stabilized by a combination of covalent and hydrogen bonds. Prior work by others has shown that cyclic peptides can self-assemble to form supramolecular assemblies through backbone-backbone hydrogen bonding. To improve upon this molecular architecture, we develop a synthesis route to polymerize cyclic peptides and form a linear polymer chain that can transition between a rigid nanorod and a “soft” unfolded conformation. For a cyclic peptide polymer containing amine-terminated side chains on each ring, we demonstrate that self-assembly can be triggered in aqueous solutions by varying the pH. We measure the elastic modulus of the rigid nanorods to be ca. 50 GPa, which is comparable to our molecular dynamics (MD) prediction (ca. 64 GPa). Our results highlight the uniqueness of our molecular architecture, namely its exemplary toughness (up to 3 GJ m⁻³), in comparison to other cyclic peptide-based assemblies. Finally, we demonstrate that the amphilic cyclic peptide nanoropes are capable of inserting into the membrane of both gram-negative and gram-positive bacteria, and causing their deaths by disrupting their osmotic pressure.

2:15 PM SM07.02.03  
Biomolecules for Non-Biological Things—Materials Construction Through Peptide Design and Solution Assembly  

Darrin J. Pochan; University of Delaware, Newark, Delaware, United States.

Self-assembly of molecules is an attractive materials construction strategy due to its simplicity in application. By considering peptide molecules in the bottom-up materials self-assembly design process, one can take advantage of inherently biomolecular attributes: intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicity, to define hierarchical material structure and consequent properties. A new solution assembled system comprised of theoretically designed coiled coil bundle motifs will be introduced. The molecules and nanostructures are not natural sequences and provide opportunity for arbitrary nanostructure creation with peptides. With control of the display of all amino acid side chains (both natural and non-natural) throughout the peptide bundles, desired physical and covalent (through appropriate “click” chemistry) interactions have been designed to produce one and two-dimensional nanostructures. One-dimensional nanostructures span exotic rigid rod molecules that produce a wide variety of liquid crystal phases to semi-flexible chains, the flexibility of which are controlled by the interbundle linking chemistry. The two dimensional nanostructure is formed by physical interactions and are nanostructures not observed in nature. All of the assemblies are responsive to temperature since the individual bundle building blocks are physically stabilized coiled coil bundles that can be melted and reformed with temperature. Additional, novel nanostructures to be discussed include uniform nanotubules as well as the templated growth of metallic nanoparticle on and in peptide nanostructures. Included in the discussion will be molecule design, hierarchical assembly pathway design and control; click chemistry reactions; and the characterization of nanostructure as well as inherent material properties (e.g. extreme stiffness, responsiveness to temperature and pH, stability in aqueous and organic solvents).

2:30 PM SM07.02.04  
Solution-Free Fabrication of Robust Silk Materials  

Chengchen Guo, Chunmei Li and David L. Kaplan; Biomedical Engineering, Tufts University, Medford, Massachusetts, United States.

Silk fibers produced by silkworms and spiders are protein-based biomaterials with a combination of excellent mechanical properties and biocompatibility. Due to these attributes, silk-based biomaterials are useful for fabricating bio-devices with important functional performance. Considerable effort has been made in developing techniques to process native silk fiber materials into silk solutions, including aqueous and solvent systems. These solutions can then be processed to generate a variety of regenerated silk materials such as films, foams, sponges and tubes. However, the tendency of silk fibroin to self assemble in solution can result in some limitations in terms of process control windows. To overcome these potential limitations and offer additional processing options for silk materials, new solution-free methods based on lyophilized silk powders help. Further improvements could be made by using silk as a raw material from the start, avoiding the complexities of processing windows and also the addition of lyophilization steps. Such processes could lead to new silk-based materials such as for films, plates, screws, bricks, and sponges prepared with tunable mechanical properties. Such a new approach should impact the field of silk device fabrication by providing new processing routes for the protein and avoiding some of the challenges with more traditional options.

2:45 PM SM07.02.05  
Natural Materials for Daytime Radiative Cooling—An Example of Regenerated Silk Fibroin Film  

Yu-Hsuan Chen¹, Dehui Wan² and Hsuen-Li Chen²; ¹Institute of Biomedical Engineering, National Tsing Hua University, Hsinchu, Taiwan; ²Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan.

Natural materials have been widely explored and applied in various fields, especially for biomedical applications. Nowadays, problems of energy crises and climate change pose a threat to human living. The consumption of energy leads to greenhouse gas emission, which causes global warming. Therefore, developing eco-friendly cooling systems is the significant issue that people are still working on. However, most of the current cooling methods needs energy to carry heat away. Radiative cooling is a passive cooling method which can lower the temperature without any energy consumption. It means that the heat can radiate to outer space through a transparency window of the atmosphere between 8-13 μm. In the past, radiative cooling during nighttime has been studied. Radiative cooling during daytime, however, is more difficult to achieve because the cooler needs to have not only high emissivity in the atmosphere windows but high reflectivity in the solar spectrum. Recently several methods have been applied to daytime radiative cooling. For example, photonic solar reflector and thermal emitter, such as HfO₂ or SiO₂ and metamaterial film, can reflect incident sunlight while emitting in the atmosphere windows. However, nano-photonic approaches require complicated fabrication and high cost, which is difficult to scale up to meet the requirements of commercial applications. While the radiative cooling technology based on natural materials is still not well studied, natural materials may have the great potential for applying on daytime radiative cooling devices.

Herein, we studied different kinds of natural materials, such as seashell, wood, bamboo and cocoon. All samples were cut into 2 x 2 cm² for optical measurements. Interestingly, all of them displayed very high absorption (i.e., high emissivity, > 80%) in broadband IR wavelength range (8-25 μm), which were mainly attributed to their intrinsic chemical
composition, such as proteins, cellulose, minerals and some small molecules due to their vibrational transitions. Noteworthy, compared to the typically narrow IR emissivity peaks of artificial daytime cooling materials, the extremely broadband emissivity peak of the natural materials could cover two atmospheric windows (8-13 μm and 16-25μm). The result means they could transfer more heat to outer space via thermal radiation and consequently are able to more efficiently lower the temperature. Among the natural materials, silk cocoon was chosen for further investigation because of its 90% absorption at IR wavelengths and the simple, well-studied fabrication process for different morphologies. We fabricated silk fibrils (SF) thin films from natural cocoon threads using the reported protocol. By adjusting the concentration of SF solution, the thin films with different thickness of 10 and 20 μm could be obtained for optical measurements. We observed that the 20-μm SF film shows a higher average emissivity of 70 % in the atmosphere windows region than the average emissivity of 50 % for the 10-μm SF film, indicating that the film thickness is a key factor. Thus, we performed a thin-film optical simulation to find the optimal thickness for the SF film. Finally, we found that the emissivity gradually increased with thickness and reached a maximum value of 95 % as the thickness of 100 μm. Further optical analyses and cooling temperature measurements for the optimized SF films are in progress and will be reported at the conference. Also, other natural materials and their optical properties as well as cooling capacity evaluations will be reported.

3:00 PM BREAK

3:30 PM *SM07.02.06

Rational Engineering of Protein-Based Biomaterials Using Folded Globular Proteins—From Single Molecule Features to Macroscopic Traits Hongbin Li; University of British Columbia, Vancouver, British Columbia, Canada.

Elastomeric proteins function as molecular springs in their biological settings to establish elastic connections, and provide mechanical strength, elasticity and extensibility. To fulfill their biological functions, elastomeric proteins have evolved to assume different structures, from simple random coil-like structure to more sophisticated beads-on-a-string conformation, and exhibit distinct mechanical properties. The development of single molecule force spectroscopy techniques has made it possible to directly probe the mechanical properties of such elastomeric proteins at the single molecule level and allowed to understand molecular design principles of these complex protein polymers. This knowledge has enabled us to engineer novel elastomeric proteins to achieve tailored and well-defined nanomechanical properties. Going a step further, we have started to employ these novel elastomeric proteins as building blocks to construct protein-based biomaterials, which in turn provide an ideal system to understand how single molecule nanomechanical features are translated into biomechanical properties of macroscopic materials. These studies will pave the way to utilizing proteins as building blocks to engineer new generations of protein-based biomaterials for diverse applications in biomedical engineering as well as material sciences.

4:00 PM SM07.02.07

Biometric Dynamic Supramolecular Assembly of Peptide Nanostructures Erik D. Spoerke; Jeffrey Vervacke, Brad Jones, Derek Nelson, Sara Russo, Bollinger Jonathan, Mark Stevens and George Bachand; Sandia National Laboratories, Albuquerque, New Mexico, United States.

Supramolecular filaments, such as microtubules (MTs), are key elements behind many of the dynamic and responsive behaviors in biological systems. In particular, MTs enable key processes ranging from intracellular cargo manipulation or changing the shape of a cell to separating genetic materials during cell division. MTs undergo a remarkably dynamic, often cyclic, assembly and disassembly process, known as dynamic instability. Key to the dynamics of the MT system is the balance between the driving forces behind MT assembly and the destabilizing influences that lead to MT depolymerization. While MT assembly is driven by a complex series of intramolecular attractive forces that bring together the tubulin heterodimer building blocks, destabilization of these attractive forces by changes in tubulin molecular shape, variations in temperature, or molecular interference with tubulin binding will cause the MTs to disassemble. Here, we explore how these concepts affect supramolecular assembly of synthetic peptides, based on the tubule-forming peptide, diphenylalanine (FF). We specifically discuss how this system mimics biological concepts of inherent supramolecular instability. We further show how the systematic incorporation of light-responsive, shape-changing azobenzene derivatives enables the use of variable molecular morphology to controllably change both to the stability and morphology of self-assembling peptide nanostructures. Through microscopic and spectroscopic characterization of systematically-modified FF peptide assemblies, we explore the mechanisms behind this dynamic behavior. Taking inspiration from such natural systems, we can learn to control critical, competitive molecular influences that regulate dynamic materials assembly. Understanding these processes will advance the development of new classes of adaptive and reconfigurable materials.


4:15 PM SM07.02.08

Vibrational Spectroscopy of Nanofibrillar Spider Silk Qiue Wang¹, Patrick McArdle², Stephanie Wang², Ryan Wilmington², Doyle Weishar³, Zhen Xing³, Muntaz Qazibush³ and Hannes Schniepp¹; ¹Applied Science, The College of William & Mary, Williamsburg, Virginia, United States; ²Physics, The College of William & Mary, Williamsburg, Virginia, United States.

The origin of spider silk’s superior mechanical properties has been intensively studied for several decades. It is widely accepted that such appealing properties originate from the hierarchical structure of silk threads. Although the protein sequence and macroscopic morphology of the silk fiber are well known, our understanding regarding structural organization for length scales in between is still limited. Nanofibrils have been suggested as an important building block in this intermediate length scale. However, no consensus model regarding their concentration in spider silk fibers or even their dimensions has emerged, which has hindered a systematic analysis of these materials. We study the silk ribbons (major ampullate (MA) silk) of the recluse (Loxosceles) spider, which entirely consist of 20-nm thin nanofibrils. This much simpler silk system thus provides an excellent opportunity to study its structure-property relations. Having performed polarized Fourier transform infrared (FTIR) and polarized Raman spectroscopy on single fibers of this silk, we know that the spectra stem solely from nanofibrils. This has allowed us to quantitatively relate the relative orientation and volumetric percentage of β-sheets vs. other types of protein secondary structures directly. Hence, our approach provides a path toward a significantly improved understanding of the structure of this protein-based material and useful insights towards replicating its merits in synthetic fibers.

4:30 PM SM07.02.09

Nanoscopic Structures and Morphological Phase Transitions in a Quaternary System of Fatty Alcohol and Cationic Surfactant Emily Wonder¹, Sumanth N. Jamadagni², Fred C. Wiroko¹, Haoran Song¹ and Cursy Safinya¹; ¹Materials, Physics, Molecular, Cellular, and Developmental Biology Departments, University of California, Santa Barbara, Santa Barbara, California, United States; ²Sharon Woods Innovation Center, The Procter & Gamble Company, Blue Ash, Ohio, United States; ³Mason Business Center, The Procter & Gamble Company, Mason, Ohio, United States; ⁴Singapore Innovation Center, The Procter & Gamble Company, Singapore, Singapore.

Surfactants and lipids are used in a broad range of applications from basic science to industrial cosmetics, hygiene, and food products. Here, we report on the structure and phase behavior of a system of two fatty alcohols (FA) and a monovalent cationic surfactant (CS). This system provides an excellent opportunity to study its structure-property relations. Having performed polarized Fourier transform infrared (FTIR) and polarized Raman spectroscopy on single fibers of this silk, we know that the spectra stem solely from nanofibrils. This has allowed us to quantitatively relate the relative orientation and volumetric percentage of β-sheets vs. other types of protein secondary structures directly. Hence, our approach provides a path toward a significantly improved understanding of the structure of this protein-based material and useful insights towards replicating its merits in synthetic fibers.

4:45 PM SM07.02.10

Self-Assembly of Peptides Nanostructures, Characterization and Neuronal Proliferation Prathvushakrishna Machu², Vikas Soni¹, Mariaris Meyes¹ and Milana C. Vasudev³; ¹Georgetown University, Washington D.C., Virginia, United States; ²Bioengineering, BMEBT, University of Massachusetts, Dartmouth, Massachusetts, United States; ³Chemistry and Biochemistry, University of Massachusetts, Dartmouth, Massachusetts, United States.
Self-assembly, involves assembly of molecules into ordered structures to various structures based on different conditions. Self-assembly of structures using biomolecules such as aromatic dippeptides, give rise to functional and biocompatible nanostructures of various forms and biomedical applications. We have synthesized nanotubes using solution-phase self-assembly (SPSA) and plasma enhanced chemical vapor deposition (PECVD), an eco-friendly technique. Quantum chemical computational methods at different levels of theories like dispersion-corrected density functional and Moller-Plesset perturbation were employed to draw insights into the self-assembly process and forces involved.

The biophysicalchemical surface properties of SPSA and PECVD nanotubes were examined using various techniques. Confocal, scanning electron and transmission electron microscopy were used to know the morphological features of these nanostructures. Thermal characterization was carried out using differential scanning calorimetry and thermogravimetric analysis, whereas the chemical characterization was done using Fourier transform infrared spectroscopy, Raman scattering, liquid chromatography-mass spectroscopy, and nuclear magnetic resonance, and circular dichroism spectroscopy, and powder x-ray diffraction. The rat adrenal pheochromocytoma (PC-12), human bone marrow neuroblasts (SH-SY5Y) and neural progenitor cells were used for cytotoxicity studies with MT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide), real-time polymerase chain reaction (q-PCR), and dopamine-enzyme linked immunosorbent assay. The differences in proliferation and expression of the cells on various samples were observed.

SESSION SM07.03: Poster Session: Bioinspired Materials—From Basic Discovery to Biomimicry
Session Chairs: Matthew Harrington, Niels Holten-Andersen and Ali Miserez
Tuesday Afternoon, April 23, 2019
5:00 PM - 7:00 PM
PCC North, 300 Level, Exhibit Hall C-E

SM07.03.01
Mechanically Manipulation Assisted Assembly of Monolithic 3D Structures from Elastomer Composites
Zheng-Wun Su1, Jiantian Li1, Jiang Liu1, Zhiyang Wang1, Yanbing Zheng1, Jianjiang Chen1, Zhen Xu2

Mechanically guided assembly is considered as a facile and scalable methodology for fabrication of three-dimensional (3D) structures. However, most of the previous methods require multiphase processes for bonding bi- or multi-layers and only result in non-freestanding 3D structures due to usage of a supporting elastomer substrate. Herein, we report a functional elastomer composite that can be transformed to a freestanding and monolithic 3D structure driven by the mechanically guided assembly. Photolithography can be used to selectively tune the mechanical properties of the exposed regions, which exhibit enhanced elasticity compared with the non-exposed regions. Thus, a gradient of the residual strain in the thickness direction makes the films assemble into 3D structures. These 3D structures are also predicted by our computational models using finite element simulations, which yields a reasonable agreement with the experiments. The system designed 2D structures with varied patterns can be transformed to various 3D structures with the control of the residual strain gradient, via key processing parameters including pre-strain, film thickness, and UV exposure time. By integrating different active electronic components on the fabricated 3D structures, potential applications of this 3D platform in electronics were demonstrated. This study offers a unique capability in constructing monolithic and freestanding 3D assembly, paving new routes to many applications such as wearable electronics, soft robotics, and structural health monitoring.

SM07.03.02
Bioinspired Metal Recovery Using Tannin-Coated Porous Substrates Under Solar Irradiation
Jeong Kim, Kyeong Rak Kim and Yoon Sung Nam

Metal ion recovery from industrial wastewater and electronic waste has attracted increasing attention to recycle precious metals and inhibit emission of hazardous heavy metals. The recovery of the precious metals has been particularly emphasized with a concept of urban mining, which aims to recover precious metals from waste resources. However, current technologies for metal recovery are not cost-effective and environmentally friendly. Recently, bioinspired coating materials have been actively investigated as metal adsorbents. In particular, polyphenols can easily produce excellent coating layers at a low cost and form coordination complexes with various metal ions, which can be used to recover precious metals from the waste. Here, we report a porous bioinspired polyphenolic adsorbent for gold recovery enhanced by light illumination. Mesoporous polymeric microspheres were employed as a porous substrate providing high specific surface area enough to efficiently adsorb gold ions. The polymer substrate was coated with tannin acid via hydrogen bonding, which leads to the coordination of gold ions with galloyl moieties and subsequent photochemical reduction of gold ions. Metal selectivity of the tannin-coated microspheres was investigated using an aqueous mixture of various metal ions. The light-enhanced adsorption and reduction of gold ions were investigated under 1 sun-simulated illumination using adsorption isotherm models. The light-enhanced adsorption and reduction of gold ions was initiated by ligand-to-metal charge transfer mainly due to UV light absorption by tannin acid, and then visible light absorption by the surface plasmon resonance of metallic gold nuclei created additional driving force for the selective reduction of gold ions. This work suggests a new design of environmentally friendly metal adsorbents for efficient noble metal recovery with a low cost by harnessing the solar energy and bioinspired coatings.

SM07.03.03
Manufacturing Biomimetic Surface with Zinc Oxide-Silver Hierarchical Nanostructures for High Efficiency Water Harvesting
Na Kyong Kim, Dong Hee Kang, Jiyoung Shin and Hyeon Wook Kang

Fresh water collecting technology from fog that known as fog harvesting is one of the solutions to solve water shortage problem specially at desert areas. In this study, we investigate an efficient water collection on a superhydrophilic surface with patterned hydrophobic regions to mimic the *stenocara* beetle surface. Superhydrophilic surface is synthesized on silicon wafer by growth of vertically aligned zinc oxide (ZnO) nanowires. The contact angle of the surface of ZnO nanowires shows 0 degree that is nucleating sites for metal salts. The final BC-curli hybrid membrane decorated with magnetite nanoparticles shows a magnetic response. The surface morphology of the hybrid material was characterized through FESEM and distribution and shape of the nanoparticles was characterized through TEM. The chemical structure and inorganic phase were characterized by FTIR and XRD respectively. Magnetic response of the hybrid material was measured using VSM.

SM07.03.04
Bioengineered Magnetic Bacterial Cellulose Membrane
Vishnu Vadanan Sundaravadanam and Sierin Lim

Bioinspired design develops new solutions in fields that conventionally have few connections with biology. Functional membrane developed through this design approach incorporates natural systems with inorganic compounds to display various functionalities, such as conductivity, magnetism, and hydrophobicity. Bacterial cellulose (BC) membrane produced by *Glucosacetobacter* species forms the skeletal framework and aids in entrapping recombinant *E. coli* bacteria. The recombinant *E. coli* bacteria containing the genetic circuit tuned to produce extracellular amyloid protein, curli, with specific functional peptides. The curli protein in the BC-curli hybrid facilitates the synthesis of magnetite nanoparticle at temperatures below 100 °C by acting as an *in situ* nucleating sites for metal salts. The final BC-curli hybrid membrane decorated with magnetite nanoparticles shows a magnetic response. The surface morphology of the hybrid material was characterized through FESEM and distribution and shape of the nanoparticles was characterized through TEM. The chemical structure and inorganic phase were characterized by FTIR and XRD respectively. Magnetic response of the hybrid material was measured using VSM.
Bioinspired Ionic Diode Membrane with High Ionic Selectivity

Jaehun Jeong1, Jongyoung Kim1, Iluk Kang2 and Kiwoon Choi2; 1NextE&M Research Institute, Incheon, Korea (the Republic of); 2Nano Research Division, National NanoFab Center, Daejeon, Korea (the Republic of).

Biological ion channels embedded in cell membranes with multiple functions have gained attention. Bacterial outer membrane protein F (OmpF) is a multifunctional channel with ionic selectivity, ionic gating, and ionic rectification properties. Also, this plays critical roles in life processes, including maintaining intracellular acidity, keeping osmotic balance, participating in ion exchange, etc. Membranes mimicking these ion channels have important applications in materials science. For practical applications, bioinspired heterogeneous membranes, which generally refer to the composite porous membrane formed by the hybridization of two functional membranes with different chemical composition, have drawn enormous research attention because of their simplicity and potential applications in mimicking various functions of biological ion channels. With respect to maintaining high mechanical strength and promoting the functionality of the fabricated membranes, organic/inorganic hybrid heterogeneous membranes represent an ideal candidate. Here, we prepared a multifunctional heterogeneous membrane by combining a sulfonated tetrafluoroethylene based fluoropolymer-copolymer membrane, Nafion, and a porous anodic aluminum oxide membrane. Despite the morphology of the as-prepared membrane is not nearly as refined as that of the OmpF, we have demonstrated a bioinspired multifunctional heterogeneous membrane capable of achieving high ionic rectification and highly efficient cation-selective gating. We expect that greater levels of multifunctionality can be implemented by optimizing the morphology of the used Nafion, thereby opening new applications in energy conversion, filtration, desalination, etc.

SM07.03.06
Inducing Fluidity in Short Chain, Amphiphilic Block Copolymer Bilayer Membranes via Polymer Functionality

Randolph J. Braun1, Anthony McNeill2, Harrison W. Reid3, Gregory H. Uyeda4, Benjamin P. Thiesing5, Stacy M. Copp6 and Gabriel A. Montano7; 1Northern Arizona University, Flagstaff, Arizona, United States; 2Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Amphiphilic block copolymers can (ABC) self-assemble into bilayer or monolayer membranes on surfaces. Relatively low molecular weight ABC bio-inspired membranes have previously been reported to be fluid as monolayer but immobile as bilayer membranes. (Goertz et al.) In this study, we investigate low-molecular weight polybutadiene-b-polyacrylic acid (pBD-b-pAA) and polybutadiene-b-polyethylene oxide (pBD-b-pEO) bilayer fluidity as a function of pH. pBD-b-pAA demonstrates the ability to generate fluid bilayers while pBD-b-pPEO bilayers are immobile as previously reported. We investigate the mobility of these short chain ABCs as a function of pH and propose a mechanism for induced fluidity in ABC membranes. Fluorescence recovery after photobleaching (FRAP) and in-situ Atomic Force Microscopy (AFM) are used to characterize the membrane compositions and their functional properties. We report our findings and the potential for generating mobile polymer membranes that more closely mimic fluid bilayers similar to those in biological lipid systems.

Reference:


SM07.03.07
Dynamic Wetting of a Droplet on Striped Surfaces

Liang He1,2 and Wenyen Liang1; 1Harbin Engineering University, Harbin, China; 2Bioresource Engineering, Montreal, Quebec, Canada.

Anisotropic wetting of natural creatures like butterfly wings, rice leaves, or bird features have received significant attention due to their potential applications, which include drop transport, microfluidics, and soft robots. The fabrication of surfaces that exhibit anisotropic wetting can be divided into two categories: chemical or geometrical patterns. Considerable effort has been made for understanding the anisotropy in wetting by both experimental and theoretical manners. However, the dynamic wetting behavior of anisotropic wetting is still in initial stages, especially in the theoretical aspect.

Here we present a thermodynamic analysis for the dynamic wetting of anisotropic wetting with the assistance of the Surface Evolver. Two analytic methods are proposed. One method involves simulation of the spreading process of a droplet on anisotropic surfaces. By keeping the droplet volume unchanged, this method is able to predict the maximum advancing contact angle, minimum receding contact angle, and the maximum contact angle hysteresis. In another method, the experimental measurement of dynamic contact angles is simulated with Surface Evolver. By increasing/decreasing the droplet volume and analyzing the wetting stability of the droplet, the minimum advancing contact angle, maximum receding contact angle, and minimum contact angle hysteresis can be determined. Additionally, the variations of droplet shape, three-phase contact line shape, and contact angles with the evolution processes in the two analytic methods are investigated.

Combining the above mentioned analytic methods, the theoretically predicted ranges of dynamic contact angles of anisotropic wetting can be narrowed. This work is also expected to provide guidance for designing surfaces with anisotropic wetting property.

(This work is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

SM07.03.08
Bioinspired Self-Morphing Hydrogel Programmed by Periodical Stiff Patterns

Heng Deng and Jian Lin; University of Missouri, Columbia, Missouri, United States.

By exploiting the spatial distribution of stiff segments in the soft tissues, plants can achieve complex shape transformations in response to external stimuli. Such natural prototype has inspired biomimetic self-morphing systems by arranging stiff segments in soft polymer matrix. Despite much progress in this research field, it is still very challenging to precisely control the distribution of the stiff segments in soft polymer matrix. As a result, the obtained self-morphing materials could only achieve very simply programmable motions such as bending, folding and twisting. To realize more complex shape changing, typical stiff segments should be delicately incorporated in selective domains of soft polymer matrix. Herein, we report a novel self-morphing system, in which non-shrinkable stiff SU-8 segments are precisely and periodically positioned in highly shrinkable soft hydrogel. Firstly, the photosensitive SU-8 is processed into discontinues periodical patterns with arbitrary designs through regular photolithography. Then the stiff SU-8 patterns are laterally stitched with tough PNIPAm hydrogel by chemical bonding, which would overcome the interfacial mechanical mismatch during the following shape transformation process. Upon dehydration, shrinkage of the hydrogel is constrained by stiff SU-8 patterns, which rises laterally nonuniform strain to create 3D structures. Such shape-changing behaviors are encoded synergetically by the soft-stiff mechanical mismatch and also the geometric periodicity of stiff patterns. By tuning the geometries of SU-8 patterns, we demonstrate a series of elegant reversible 3D shapes, such as alternating concave-convex configurations, 3D checkerboard patterns and other Gaussian curvature surfaces.

SM07.03.09
Extraction and Characterization of Ferulated and High-Methoxyl Pectins from Sugar Beet

Claudia Lara-Espinoza, Elizabeth Carvajal-Millan, Alma Campa-Mada, Jorge Alberto Manquez-Escalante, Jose Alfonso Sánchez-Villegas and Agustín Rascon Chu; Centro de Investigacion en Alimentacion y Desarollo, Hidalgo, Mexico.

Ferulated pectins have polysaccharides from the cell wall of dicotyledonous plants and consist of linear polymers formed mainly by galacturonic acid units linked glycosidically by α-(1,4) bonds. Traditionally, pectins are extracted from citrus peels and apple pomace, although they can also be recovered from minor sources such as sugar beet which have particular structural characteristics, like the presence of ferulic acid bound to galactose and arabinose residues, which enables oxidative coupling between polysaccharide chains. Ferulated pectin gels have become relevant in the design of matrices for the controlled release of molecules of therapeutic interest. In the present study, ferulated pectin was extracted from a sugar beet cvr. grown in Mexico, and composition and physicochemical characteristics were investigated. Pectins presented a galacturonic acid content of 63% (w/w) and residual sugar beet cvar. grown in Mexico, and composition and physicochemical characteristics were investigated. Pectins presented a galacturonic acid content of 63% (w/w) and residual sugar beet cvar. grown in Mexico, and composition and physicochemical characteristics were investigated. Pectins presented a galacturonic acid content of 63% (w/w) and residual

SM07.03.10
Highly Ferulated Arabinoxylans as Gelling Agents Presenting Antioxidant Activity—The Central Role of Ferulic Acid Content

Ana Maria Morales-Burgos1, Elizabeth J. Queguiner1,2, Benjamín P. Thiesing3, Jongyoung Kim4 and Gabriel A. Montaño5; 1International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation; 2Harbin Engineering University, Harbin, China; 3Bioresource Engineering, Montreal, Quebec, Canada; 4Mechanical Engineering, National Institute of Technology, Mexico; 5Zoology, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.
Effective antimicrobial surface coatings are critical from both economic and health perspectives. In the present study, we aimed to design novel adhesive antimicrobial peptides (AMPs), based on adhesive proteins in mussels, for one-step coating without the need for prior surface functionalization. In the system, we modified the sequence of a potent synthetic AMP, NKC, with additional repeats of an unnatural amino acid, 3,4-dihydroxy-L-phenylalanine (DOPA), at the C-terminus and evaluated their adhesiveness and antibacterial properties depending on the number of DOPA moieties, using the biochinchonic acid assay and minimum inhibition concentration (MIC) test. The peptide containing 7 DOPA residues aggregated excessively and exhibited higher MIC values than NKC-DOPA. Surface characterization assays such as X-ray photoelectron spectroscopy and atomic force microscopy confirmed that NKC-DOPA was successfully immobilized onto the surfaces of polystyrene, titanium, and silicone, when treated with NKC-DOPA solution for 10 min. The antibacterial effect of NKC-DOPA coating was evaluated via a colony formation assay and the peptide-coated surfaces revealed 99.99% growth inhibition of 10° cells of Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus aureus within 2 h. In addition, NKC-DOPA-immobilized surfaces retained their antibacterial activity for at least 84 days. NKC-DOPA-coated polystyrene, titanium, and silicone catheters displayed no cytotoxicity on a human keratinocyte HaCaT cell line, on an MTT assay, thereby indicating a promising biocompatibility. Furthermore, this coating method involves water-based solutions, which are compatible with most surfaces and are environmentally compatible. Overall, the adhesive AMPs developed in this study have high potential for their use as antimicrobial coating agents to prevent material surfaces from bacterial colonization. This study was supported by the Intelligent Synthetic Biology Center of Global Frontier Project funded by the Ministry of Science and ICT of Korea.

SM07.03.12 Production Conditions to Control Mechanical Properties of BC Membrane Florentina Sederaviciute1, Jurgeita Domskienė1 and Paulė Bekampiene2; 1Kaunas University of Technology, Kaunas, Lithuania; 2Textile Institute, Kaunas, Lithuania.

Bacterial cellulose can be obtained through fermentation of sugared tea with Kombucha fungus. Kombucha drink is considered as health and therapeutic agent. Tea fungus is a symbiotic mixture of lactic acid bacteria and yeasts and during fermentation forms cellulose nano-fibers floating over surface. The cellulose mass with attached bacteria and yeasts is secondary metabolite of fermentation which can be utilized as supplement in animal feed or thrown as waste. Presented research analysis is about possibilities to use BC material obtained through Kombucha fermentation as alternative material for sustainable fashion. The effect of washing and chemical treatment on mechanical, structural and water barrier properties of bacterial cellulose material is analysed. The study concerns bacterial cellulose (BC) properties in three different states: 1. Untreated - as natural fermentation product from acetic acid bacteria Komagataeibacteria xylinus; 2. Pretreated - washed with water and weak alkali (0.5 %) solution; 3. Treated with dimethyl dihydroxyethyleneurea (DMHDEU) solid. Through pretreatment washing procedure fermentation side products (acids, input materials, sugars) are removed from BC membrane therefore this process has influence on material structure and properties. The structure of washed BC material can be described as coherent three-dimensional network of nanofibers with low water vapour permeability and low hygroscopicity. The decrease of deformation and of water barrier properties is recorded after BC washing. Applied chemical treatment has positive influence on properties of BC membrane (increase of material elasticity, strength, hygroscopicity and water vapour permeability) and no influence on BC structural transformation (FTIR analysis).
to gold and can offer a tool for multifaceted soft/hard nanomaterials.

9:30 AM SM07.04.03
(Multi)Functional Structured Hydrogels Inspired by ECM Andreas Lendlein1,2; 1Institute of Biomaterial Science and Berlin-Brandenburg Centre for Regenerative Therapies, Helmholtz-Zentrum Geesthacht GmbH, Teltow, Germany; 2Institute of Chemistry, University of Potsdam, Potsdam, Germany.

The extracellular matrix (ECM) is a complex hydrogel material providing multiple functions and is in this way an impressive example for integrating several functions in a material system. It still is a challenge to completely prepare ECM by synthetic methods. However specific principles for generating functions by molecular design or hierarchical organization can serve as concepts for the biospired design of structured hydrogels.

In this lecture a gelatin based porous hydrogel will be presented, which is prepared in a one step process integrating synthesis and shaping [1]. Its elastic properties on the micro- and the macrolevel can be tailored and cell behavior can be influenced. The hydrogel is also capable of a water induced shape-memory effect. The concept of shape-memory hydrogels [2] has been taken further to a triple-shape effect enabling two subsequent shape changes upon heating [3]. Finally, the application potential of multifunctional structured hydrogels will be outlined.

References:

9:45 AM SM07.04.04
Understanding of Liquid-Liquid Phase Separation of Histidine-Rich Squid Beak Proteins—First Step Towards Development of Bioinspired Functionally Graded Composite Materials Bartosz Gabryeleczk1,2, Hao Cai1, Xianguan Shi1, Konstantin Pervushin3 and Ali Miserez2; 1Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland; 2School of Materials Science & Engineering, Nanyang Technological University, Singapore, Singapore; 3School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore.

Liquid-liquid phase separation (LLPS) of intrinsically disordered proteins (IDPs) has been recently associated with formation of intracellular membrane-less organelles and extracellular load-bearing structures, including biocomposite materials. Although the biophysical principles of LLPS of various synthetic and natural polymer systems have been already well characterized, molecular interactions driving the phase separation of IDPs are still poorly understood.

Histidine-rich squid beak proteins (HBPs) are IDPs that are the main component of the beak of Humboldt squid D. gigan. The beak is an interesting example of a graded biocomposite material with remarkable mechanical properties exhibiting a 200-fold variation in stiffness from the soft base to the hard tip. It is exclusively made of chitin and proteins, i.e. lacks a mineral phase such as calcium carbonate or phosphate - the classical load-bearing component of a hard tissue. Thus, the beak represents a promising model of a fully organic material with load-bearing functions for bioinspired materials engineering.

It has been proposed that the HBPs have crucial role in the beak processing in nature due to their intrinsic ability to undergo LLPS (coacervation) that allows them to gradually impregnate chitin nanofibers scaffold in the beak, condense into a solid structure, and form a dense cross-linked network (final beak structure). By studying a model protein (HBP-1) we showed that phase separation of HBPs is mediated through modular repeats located in their C-terminal part. Using maturation approach, we mapped essential minimal peptide sequences required for LLPS to occur and showed critical role of tyrosine residues. We also demonstrated that the morphology of separated phase (coacervates/hydrogel) is correlated with the hydrophobicity of modular repeats and can be tuned by incorporation of specific sequence motifs into a peptide sequence. Utilizing solution-state NMR, we investigated initialization of LLPS of the HBP-1 protein and HBP-derived model peptide sequence (GY-23). We demonstrated that they phase separate in a pH depended process, triggered by deprotonation of histidine residues followed by stabilization of their tautomeric state by transient hydrogen bonding with tyrosine residues. We proposed that these events lead to hydrophobic inter-molecular interactions which are the main driving force of LLPS. Subsequently, we investigated separated phase (coacervates) of GY-23 peptide using SAXS and showed that it possesses internal structure in nm range which is partly ordered. Finally, we studied the molecular features of coacervate phase with solid-state NMR and showed that tyrosine residues stabilize its structure by hydrophobic interactions. Overall, this work provides essential knowledge and guidelines for rational design of pH responsive peptides with LLPS ability for engineering of bioinspired functionally graded composite materials and other applications such as smart hydrogels and drug delivery systems.

References:

10:00 AM BREAK

10:30 AM SM07.04.05
Dynamic Transition from α-helices to β-sheets in Polypeptide Superhelices Valeri Barsegov1, Prashant Purohit2, Kenneth Marx1 and Artem Zhurnov3; 1University of Massachusetts, Lowell, Massachusetts, United States; 2Department of Mechanical Engineering and Applied Physics, University of Pennsylvania, Philadelphia, Pennsylvania, United States; 3Moscow Institute of Physics and Technology, Dolgoprudny, Russian Federation.

We employed computational molecular modeling and dynamic force spectroscopy in silico accelerated on Graphics Processing Units (GPUs) to perform the mechanical manipulations at the nanoscale on a variety of superhelical protein fragments. We utilized the atomic structures of coiled-coil motifs available from the Protein Data Bank (PDB) for myosin (PDB entry: 2FXO), chemotaxis receptor (2GUV), vimentin (1GK4), fibrin (2GHG), and phenylalanine zippers (2GUS), as suitable study systems. We used the all-atom Molecular Dynamics simulations on GPUs in the underdamped (low-friction) limit in conjunction with the Solvent Accessible Surface Area (SASA) model of implicit solvation. The coiled-coil motifs listed above vary in size as well as topology of their α-helical packing. We loaded these study systems with tension linearly increasing in time, which fully mimics the tensile testing single-molecule force-ramp experiments. When stretched along the superhelical axis, all superhelices showed elastic, plastic, and inelastic elongation regimes, and underwent a remarkable dynamic transition from the α-helices to the β-sheets, which marks the onset of plastic deformation. Hence, the soft α-to-β phase transition in coiled coils is a universal mechanism underlying the mechanical properties of filamentous α-helical proteins. We analyzed in detail the output from the simulations. Microscopically, the α-helical (β-strand) content decreases (increases) with tension, and the transformation from the α-helices to the β-sheets is a two-state transition. This transition is accompanied by redistribution of the dihedral angles ϕ and ψ and reconfiguration of hydrogen bonds (from the intra-chain to the inter-chain hydrogen bonds). Using Abeyaratne-Knowles formulation of phase transitions, we developed a new theory to model the mechanical and kinetic properties of protein superhelices under mechanical non-equilibrium conditions used in tensile testing assays. We also implemented an approach to map out the free-energy landscapes of polypeptides with coiled-coil motifs, in order to resolve the critical extension and to estimate the energy difference between the α-helical state and β-sheet state per helical pitch. The developed theory was validated by directly comparing the simulated and theoretical force-strain spectra. Interestingly, we found that the coiled coils show a roughly additive contribution to the mechanical strength from α-helices, which weakly cooperate to sustain the stress. We also found that the coiled coils with parallel arrangement of their α-helices provides higher mechanical strength as compared to the coiled coils with antiparallel arrangement. The theory can be used to accurately describe dynamic transitions in wild-type and synthetic superhelical polypeptides under mechanical non-equilibrium conditions, and to model their force-strain spectra available from dynamic force manipulations in situ and in silico. The theory can be applied to any coiled-coil superhelical polypeptide, in order to probe its mechanical and kinetic properties and to map out its free-energy landscapes. The derived scaling laws for the elastic force and the force for α-to-β transition to plastic deformation provide an analytical tool to rationally design novel synthetic biomaterials and nanomaterials with the required mechanical strength and desired balance between stiffness and plasticity.

11:00 AM SM07.04.06
Higher-Order Assembly of Coiled-Coil Peptides for Biomaterial Applications Monesisha Nambiar1, Li-Sheng Wang2, Vincent M. Rotello2 and Jean Chimleiwski1; 1Purdue
The successful application of synthetic biomaterials to their ability to mimic naturally occurring biological molecules and systems. The challenge however, has always been to generate materials with hierarchical assemblies down to the atomic level that have precisely tailored chemical heterogeneities and external stimuli-responsiveness. Self-assembling peptides have recently emerged as a potential avenue for the creation of novel biomaterials because they are materials based on natural building blocks. The knowledge about their sequence-structure relationship coupled with the ability to design and synthesize de novo peptides has sparked an interest in the use of coiled-coil peptides as biomaterials in various fields; tissue engineering, drug delivery, regenerative medicine and bio-sensing to name a few. Our approach utilizes a GCN4 leucine zipper sequence-based coiled-coil trimer that has been radically functionalized with aromatic ligands to build hierarchical assemblies. These higher-order assemblies, which take the form of banded rectangular nanosheets, are formed via electrostatic and aromatic interactions. The dimensions and overall shape of these assemblies vary with the strategic placement and number of aromatic ligands on the monomer backbone. Their assembly was observed to be reversible and can be controlled by adjusting the pH of the solvent medium. Additionally, the unmodified variant of the peptide resulted in the formation of microtubes. Our work showcase how small changes in the peptide sequence can translate into distinct differences in the resulting supramolecular architecture. The possible variety of hierarchical structures make coiled-coils suitable for creating novel biomaterial scaffolds.

11:15 AM SM07.04.07
Cytoskeleton-Inspired Biopolymer Design to Reduce Topological Defects in Polymer Networks

David S. Knoff1, Haley Szczechowski1, Fathima Doole1 and Minkyu Kim2, 3, 4; 1Biomedical Engineering, University of Arizona, Tucson, Arizona, United States; 2Materials Science Engineering, University of Arizona, Tucson, Arizona, United States; 3BIOS Institute, University of Arizona, Tucson, Arizona, United States; 4Chemistry & Biochemistry, University of Arizona, Tucson, Arizona, United States.

In mechanical testing, polymers regularly underperform compared to their theoretical calculations due to defects in the network, including dangling chains, free chains, loops, and various forms of bridge entanglements. Efforts have been made to count the number of network imperfections, however, there are no current methods for reducing defects in physically-associated polymer networks. Well-organized biological networks in cell cytoskeletons contain selective binding mechanisms and rigid-structured proteins that reduce defects, inspiring our polymer network design. In this study, a novel mechanism for reducing network defects was investigated by designing protein polymer mid-blocks with rigid and flexible components in specific ratios and module arrangements.

Protein polymers were designed with a rigid rod block and various lengths of flexible coil blocks to modulate polymer chain stiffness, which can potentially control network defects. The rigid component consists of synthetic ankyrin repeats, known for its 3D solenoid structure. The flexible component includes primary-structured polyelectrolyte protein repeats. These rod and coil protein blocks were genetically inserted into a telechelic associative construct with self-oligomerizing proteins to form hydrogels. To determine the optimal copolymer design that reduces network defects, such as self-loops and dangling chains, we investigated the mechanical properties of hydrogels containing mid-blocks with varying rigid-to-flexible lengths, as well as symmetrical and asymmetrical block arrangements within each protein polymer. The incorporation of rigid components increased the elastic moduli compared to flexible controls, providing evidence that network defects can be reduced in telechelic associative polymers by manipulating chain flexibility.

11:30 AM SM07.04.08
Human Aorta Under Tensile Stress

Sabrina Friebe1, 2, Josephina Haensch1, Christian Ett1 and Stefan Mayr1, 2; 1University of Leipzig, Leipzig, Germany; 2Leibniz-Institut für Oberflächenmodifizierung (IOM) e.V., Leipzig, Germany.

An aortic aneurysm constitutes a local enlargement of the aorta that is identified incidentally in most patients due to absence of symptoms. Prevalence of this disease strongly depends on age, gender and distinct risk factors, including smoking, overweight, hypertension and increased level of blood lipids. In case of an increasing aneurysm diameter, rupture within the aortic wall is an acute threat, so the called aortic dissection. At worst, rupture of the entire aorta arises, the so called aortic rupture. Within an interdisciplinary approach we investigate aortic samples from patients who suffer from an aortic aneurysm and underwent a surgery with regard to their mechanical properties. In doing so, tubular aortic portions were harvested from patients and cut into rectangular shapes, originated from convex, concave and longitudinal parts of the aorta, and stretched until rupture. Clinical data of patients as age, aortic diameter, arterial hypertension, elastin and collagen content or type of aortic valve (bicuspid- or tricuspid aortic valve) were correlated with the Young's modulus to contribute to a better understanding of the role of pathological factors in mechanical properties of aorta.

11:45 AM SM07.04.09
Wrinkling 2.0—Methods for Defect and Crack Prevention, Variation of Employed Materials and Upscaling

Bernhard Glatz, André Knapp and Andreas Fery; Leibniz Institute of Polymer Research Dresden, Institute of Physical Chemistry and Polymer Physics, Dresden, Germany.

Wrinkles form, when a system consisting of a hard, thin layer in strong adhesive contact with a soft, thick elastomer is subjected to in-plane compression, just like skin that wrinkles or mountain ranges that fold. The arising buckling instability can be unrepairable, or a highly periodic surface corrugation with well-defined wavelength and amplitude, when a defined stress-field is applied. Manifold preparation methods are known, such as metal deposition on elastomers, plasma treatment of PDMS or the adhesion of stiff polymeric layers on elastomeric sheets. However, most methods are limited in terms of material and parameter variety, only few perform with more than one elastomer or thin layer material, respectively. Also they comprise side features as cracks and line defects, which form in most wrinkling process and are unpredictable yet. Furthermore, controlled wrinkling is still limited to small size ranges in the square millimeter- and centimeter-range. [1]

We demonstrate a new approach, where line defects are confined and subsequently arranged by modifying the substrate, and cracks are suppressed by the implementation of a specific elasticity gradient. [2,3] Furthermore, we show a new approach that is applicable to versatile layer and elastomer materials, and also unlimited in terms of pattern size. [4] We show the utility of both line defect- and crack-free wrinkles, and of different layer and elastomer materials for large-scale wrinkled areas. Such highly ordered, macroscopic patterns can be applied to biologically functional surfaces, like cell- and virus-repelling material for medicine, anti-fouling surfaces in large area for diverse bio-industrial applications or friction-minimizing interfaces.

technologies are still restricted by their lack of nanopattern variability, processing area, and control of surface chemistry, especially in clinically relevant polymers. In this work, we present a method based on directed plasma nanosynthesis (DPNS) for fabricating freestanding nanopillars in a model fibrous hydrogel, i.e., bacterial cellulose (BC), with the aim of designing antimicrobial interfaces that can prevent bacterial contamination in biomedical devices. DPNS is advantageous for the large-area and short processing time as compared to FIBL and similar approaches. Nanopillars are fabricated in BC hydrogel by DPNS using argon at high fluence, normal incidence, and energies of 1 keV. BC is a natural polysaccharide formed by β-1,4-glucopyranose residues and used in biomedical applications such as wound dressing, artificial corneas, and in skin and blood vessel substitutes. The surface morphology of BC after argon plasma treatment was investigated by focused ion beam with scanning electron microscopy. Structural characterization showed that at low argon doses, the BC ribbon structure exhibited nucleation and growth of holes that progressively building-up leaving behind well-organized nanopillars at high fluences with an average height of 220 nm determined by atomic force microscopy. X-ray photoelectron spectroscopy (XPS) spectra revealed an enrichment of the C-C/H bonds and depletion of oxygen with the preferential removal of C-O bonds. The C-O/C-OH bonds also decreased drastically, whereas the C/O=C-O were only slightly reduced. Because oxygen atoms are responsible for linking the glycopyranose monomers and forming the ring structure in the BC, this would cause the restructuration of the polymer chains via ring opening and chain scissoring, driving nanopillar formation. The surface wettability of argon-treated BC measured within the first 24 h after treatment using the static water contact angle showed that this material was superhydrophilic. By tuning the energy, ion dose, and angle of incidence during DPNS treatment, we found that it was possible to custom design the pillar height and nanopillar density. In summary, the nanopillar structures obtained here in a fibrous hydrogel are of practical significance for the application in various fields such as biosensors, optoelectronics, and antibiofouling interfaces of industrial and clinical importance.

1:45 PM SM07.05.02
Engineered Polymer Nanopillars with Ultrathin Efficiency and Therapeutic Indices Against Multidrug-Resistant Bacteria and Biofilms
Akash Gupta, Ryan Landis, Cheng-Hsuan Li, Martin Schnurr, Riddha Das and Vincent M. Rotello; University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Overuse of antibiotics has created “superbugs” such as methicillin-resistant Staphylococcus aureus (MRSA) that pose serious threat to global health due to treatment failure and high mortality rates. The threat is further aggravated by chronic infections from biofilms, which exhibit high resistance towards both the host immune response and traditional antimicrobial therapy. Synthetic macromolecules have emerged as an alternative to conventional antibiotic therapy exhibiting broad spectrum activity against antibiotic-resistant bacteria. However, high toxicity towards mammalian cells and concomitant low therapeutic indices have limited their practical applications in clinical settings. Here, we report engineered polymers that can effectively eradicate pre-formed biofilms while maintaining a high therapeutic index against human red blood cells (RBCs). We synthesized a library of quaterary ammonium poly(oxanorborneneimides) possessing different degrees of hydrophobicity and screened their antimicrobial and hemolytic activities. These polymers form 10-15 mm nanoparticles in aqueous solution, increasing their overall cationic charge and molecular mass. We determined that increasing hydrophobicity of the alkyl chains bridging the cationic head group and polymer backbone greatly enhances toxicity against planktonic bacteria while maintaining excellent hemolytic activities towards RBCs (Therapeutic Index >5000). Additionally, nanoparticle polymers readily penetrate and eradicate pre-formed biofilms while still maintaining high therapeutic indices (~120) relative to RBCs. Polymeric NPs demonstrated a 6-log reduction in bacterial count in a biofilm-mammalian cell coculture model. Significantly, we observed that bacteria did not develop any resistance against polymeric NPs even after 20 serial passages. Overall, our engineered polymeric nanoparticle platform shows strong potential as an infectious disease therapeutic and simultaneously provides a rational approach to design novel antimicrobials for long-term combatting of bacterial infections.

2:00 PM SM07.05.03
Biomimetic Moisture Responsive Fabrics
Lihong Liao, Yuen Shing Wu and Jiuntu Fan; Cornell University, Ithaca, New York, United States.

A stoma (plural stomata) is a pore or opening in the epidermis of plant leaves, through which carbon dioxide is received for photosynthesis and water vapor is transpired. A stoma consists of two guard cells, having thicker and inextensible inner walls and outer walls that are thinner and more extensible. The stoma open and close through the swelling and shrinking of the two guard cells in response to environmental stimuli, e.g. high light intensity and high humidity.

In this study, we are fabricating the pores in a breathable fabric to mimic the structure and function of leaf stomata. In the artificial stomata, a special polymer is coated around a slit (“pore”) of the fabric to form “guard cells”. The polymer will bend asymmetrically toward one side under higher humidity (wet), leading the “pore” to open, while it stays still under normal humidity (dry) which keeps the “pore” close. In both conditions, the fabric maintains a flat surface without buckling, which means little effect on the overall dimension of the fabric.

The process is simple and easy to scale. The polymer can be coated via digital liquid dispensers, or various industrial printing techniques, like screen printing or 3D printing. The slit can be cut by laser etching technology, and the dimensions can vary from micro- to millimeters. The dimension change of the pore under “open” and “close” states can be easily measured by the length and wide change, or observed under optical microscope. The fine structure and morphology can be examined under scanning electron microscope (SEM). The air penetration or vapor transmission through the pores can be measured by air permeability tester (e.g. KES-AP) or moisture vapor transmission rate (MVTR) tester.

2:15 PM SM07.05.04
Deposition Control of LC Polysaccharide at Evaporative Interface to Design Quickly Swelling Oriented Hydrogels
Gargi Joshi1, Kosuke Okeyoshi2, Tetsu Mitsumata2 and Tatsuo Kaneko1;1 Japan Advanced Institute of Science and Technology, Nomi, Japan;2 Niigata University, Niigata, Japan.

[ABSTRACT]

Self-assembly of polymeric liquid crystals (LC) has emerged as a powerful technique to recreate the complex hierarchy found in nature, from simple building blocks. Evaporation is often employed as a driving force to initiate the assembly of LC domains in the solution. By tuning the conditions of drying, it is possible to gain control over their mobility and in turn on the orientation during deposition. Recently, our group reported a macropore-partitioning phenomenon upon drying a polysaccharide aqueous LC solution from a limited evaporative interface.1,2 Vertical membranes were deposited, bridging a millimeter-scale gap between the substrates and formed a highly oriented structure as a result of a non-equilibrium process between polymer deposition and hydration. In this study, in order to generalize this space-partitioning phenomenon and explore structural changes due to temperature variations, we have explored the drying of xanthan gum solution. It is a cholesteric LC polysaccharide commercially used in food industry, cosmetic formulations and as a viscosity enhancer. Most importantly, xanthan gum LC state is intrinsically affected by changes in temperature. By varying the conditions of temperature and initial concentration, the depositions induced in the limited space have been monitored and a comparative phase diagram prepared.3

We observed deposition of a horizontal lid-like membrane preceding the growth of vertical membrane. The restrained availability of space led to a dense layer at the drying interface which resulted in the deposition of this lid structure. To clarify the microstructures of these membranes, the lid and the vertical membrane retrieved after drying xanthan solution at 60 °C were scrutinized in three dimensions. The deposited membranes exhibited an arrangement of fibrous structures with orientations dictated by the experimental conditions and LC mobility. The SEM images showed that the membrane is composed of fibres with ~50 nm diameter in orientation. We also prepared a phase diagram, focusing on the initial polymer concentration, C0 and drying temperature to clarify the effect of the domain’s mobility on the bridging deposition.

Furthermore, the introduction of crosslinking points in the membranes, by annealing at a higher temperature resulted in the formation of oriented hydrogels with quick and reversible anisotropic swelling. Such hydrogels with inherent biocompatibility and fast response rate have great demand for drug delivery, tissue engineering, and biomimicking applications. The imitation of condensation by drying in this work will provide not only a gain in understanding of the self-organization of biopolymers in living systems but also a simplified methodology to design self-assembled biomimetic materials with highly-ordered structures.

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3. G. Joshi, K. Okeyoshi, T. Mitsumata, T. Kaneko. Submitted

[ACKNOWLEDGEMENTS]

G. J. is grateful for the JSPS DC2 Fellowship and the JSPS Kakenhi Grant Number JP18J11881.

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Effects of Nanoparticle Composition and Size on the Crosslinking and Mechanical Behavior of Nanoparticle Hydrogels

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Materials inspired by the byssal threads of mussels are of interest for their strong mechanical properties, which are based on coordination of catechol moieties with Fe\(^{3+}\) ions. A 4-arm polyethylene glycol terminated with catechols (4PEG-c) was used to investigate the chemistry and rheology of crosslinking with a set of different compositions (Fe\(_2\)O\(_3\), CoFe\(_2\)O\(_4\), NiFe\(_2\)O\(_4\), Co, and Ni) and sizes (3-7 nm diameters) of NPs. A ligand exchange process was developed to prepare the samples for dispersion in water and coordination with 4PEG-c to form hydrogels. Raman spectroscopy showed less binding of 4PEG-c to Co- and Ni-based NPs than for Fe\(_2\)O\(_3\) NPs, but rheology measurements revealed significantly slower relaxation times for Co- and Ni-based NPs than for Fe\(_2\)O\(_3\) NPs. We attribute these results to initial binding of catechols to Co- and Ni-based NPs, which could catalyze the oxidation of catechols and drive covalent crosslinking between 4PEG-c molecules. We propose such crosslinking results in a polydopamine-like structure. Thus, Co- and Ni-based NPs can serve as catalysts, drive crosslinking, and slow the relaxation times, only while weakly binding to the catechols. These results provide a foundation for incorporating other types of NPs into synthetic, physical hydrogels and highlight the potential role of Co- and Ni-based NPs in catalyzing crosslinking of catechols.

Molecular Mechanics of Mussel Inspired Polymer Coatings

Peyman Delavarast\(^1\), Katerina G. Malollari\(^1\), Haesin Lee\(^2\) and Phillip B. Messersmith\(^3,4\); \(^1\)Materials Science and Engineering, University of California, Berkeley, California, United States; \(^2\)Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States; \(^3\)Bioengineering, University of California, Berkeley, Berkeley, California, United States; \(^4\)Lawrence Berkeley National Laboratory, Berkeley, California, United States; \(^5\)Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea (the Republic of).

Inspired by the catechol and amine-rich adhesive proteins of mussels, polydopamine (pDA) has been widely adopted for coating solid surfaces due to the versatility and simplicity of pDA film deposition. Conformal pDA films of thickness 1–100 nanometers spontaneously form at the solid-liquid interface on nearly all types of solids by simple immersion in an aqueous alkaline solution of dopamine. Little is understood about pDA film formation except that oxidation of dopamine gives rise initially to dopamine-quinone and dihydroxyindole. An open question concerns whether the final product is a covalent polymer or a supramolecular aggregate of small molecules and oligomers. We employed single molecule force spectroscopy (SMFS) to show that pDA exhibits characteristic features of a polymer with contour lengths up to 200nm. pDA chains exhibit mostly weak interactions with oxide surfaces with occasional “sticky” points along the contour length, suggestive of a copolymer structure composed of building blocks of variable composition. Our findings provide the first direct evidence for the polymeric nature of pDA, and offer a foundation upon which to better understand and tailor its physicochemical properties.

Mussel-Inspired Coatings of Mesoporous Polymer Particles for Photo-Enhanced Gold Recovery from Electronic Wastes

Kyeong Rak Kim, Jeonga Kim and Yoon Sung Nam; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Metal ion adsorption from electronic wastes (E-wastes) has received much attention for the elimination of heavy metals and the recovery of precious noble metals. However, cost effectiveness and metal selectivity still remain to be solved. Herein, we introduce a simple method to efficiently increase gold adsorption from metal ion mixtures using bio-inspired polyphenol chemistry under light illumination. Mesoporous poly(ethylene glycol dimethacrylate-co-acrylonitrile) (poly(EGDMA-co-AN)) microspheres were prepared by suspension polymerization and used as polymer templates. The internal surfaces of the polymer templates were coated by polydopamines via the oxidative polymerization of dopamines. The polydopamine layers served as a metal ion adsorbent activated by 1 sun-simulated illumination. The adsorption isotherm curves and maximum capacities of gold ions were evaluated by Langmuir, Freundlich, and BET adsorption models. The maximum amounts of chloroauric ions adsorbed per unit mass of the adsorbents under the 1 sun-simulated light were 25 times higher than the adsorbents in the dark. The gold ions could be removed from the adsorbents in a thiourea solution. Metal ions complex solutions were used to determine the selectivity of the polydopamine-coated particles for gold ions among various metal ions. High adsorption capacity and selectivity toward gold ions at a high concentration (1.5 mM) of a metal ion mixture containing six kinds of metals (Cu, Co, Ni, Pt, Pd, and Au) was demonstrated. The structural properties and the surface chemistry were investigated using SEM, TEM, XPS, XRD, and BET analysis, and the amount of gold ions were analyzed by ICP-MS analysis. Our bio-inspired approach to photo-enhanced adsorption of gold ions using polyphenol chemistry will lead to practical applications for the recycling of the precious metals from E-wastes. This research was supported by Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2017M3A7B4042235).

Hairy Graphenes—Assembling Nanocellulose Nets Around Graphene Oxide Sheets

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Self-assembly of diverse natural component is critical for biological phenomena understanding and advanced materials development; however, self-assembly of 2D heterostructural nanosheets from 1D biocolloid is extremely challenging because of complex interactions, geometrical structure, flexibility and limited processing window. Herein, we report a simple, efficient, and universal amphiphility-driven self-assembly strategy to construct 1D stiff nanocellulose into 2D flexible nanosheets with graphene oxide (GO) monolayer as template core. This self-assembly is facilitated by highly tunable amphiphilic interaction via tailoring the surface chemistry of GO nanosheets, resulting in unprecedentedly ultradense nanocellulose coverage. These as-obtained ultradense nanocellulose nanosheets demonstrated record-breaking elastic modulus cellulose nanocomposites, even comparable to single nanocellulose. Additionally, the presence of nanocellulose significantly enhances the surface wettability of hydrophobic rGO nanosheets, enabling the long-term stable rGO dispersion and allowing fast water transport through these hybrid thin films for dye and nanoparticles separation.
Fiber-reinforced materials are used increasingly in many high-end technical applications including aviation and space flight, automotive, and also for sports equipment and medical applications as e.g. for protheses and orthoses. Technical fiber-reinforced composite materials share many properties with their biological counterparts and proved to be very suitable for the fabrication of innovative biomimetic products. Examples for light-weight materials with excellent mechanical load bearing properties and an benign fracture behavior include biomimetically optimized branched fibrous composite materials with gradient structure and with or without concrete filling inspired by branched stems of dragon trees (Dracaena spp.), dwarf umbrella trees (Schefflera arboricola) and columnar cacti (e.g. Mammillaria sp. or Pachycereus sp.). However, fiber-reinforced materials systems can do much more than stiffening as well as in biology and in technology. The hierarchically structured fibrous bark of the giant sequoia (Sequoia gigantea), for example, represents not only a brilliant heat insulator and is self-extinguishing (protection against wild fires) but additionally is a very efficient and light-weight damping system (protection against rock fall). In addition, also complex motion patterns can be imprinted in the fibrous structure of fiber-reinforced plant materials systems allowing for one, two and three-phase motions. Examples include one and two phase model patterns found in pinecone scales (Pinus spp.) and three phase motions occurring in the involucral bracts of the silver thistle (Carlina acaulis). What’s more: these organs combine sensor, actuator, reactive movable element and support structure in one materials system, are entirely passive (no energy consumption), show high level of functional integration and display extraordinary high functional resilience and robustness. The latter was proven for 11.5 to 16 million years old charcoalified conifer cone scales (Keteleeria sp.) that still show the same motion pattern in hydration/dehydration cycles as their extinct counterparts. New production methods, as e.g. 3D-4D-printing or 3D-braining pulltrusion, allow to produce similar as in biology from small to big and to create a hierarchical structuring similar to that found in the biological role models. They therefore enable for the first time the transfer of many outstanding properties of the biological role models into innovative biomimetic products at reasonable costs. Based on a thorough analysis of the hierarchical structuring of the biological role models and of their scale overarchning mechanical properties these production methods will allow for the development of novel sophisticated living, adaptive and energy-autonomous materials systems. This challenge is central to the new Custer of Excellence livMatS, which has started in January 2019 at the University of Freiburg and aims to come from biinspired materials to living materials systems.

9:30 AM SM07.06.02 Enhancing Tensile Properties by Bio-Inspired Porous Arrangement—Modeling, 3D Printing, Mechanical Testing and Optimization Cheng-Chie Tung and Po-Yu Chen; National Tsing Hua University, Hsinchu city, Taiwan.

Cellular structures provide high material usage efficiency, specific strength, and energy absorption for lightweight structural materials. The mechanical properties can be maintained or increased through appropriate porous and wall designs even the material selections are limited. In this research, we focused on the enhancement of lightweight structure tensile properties based on single material. Voronoi tessellation, often appears in cells and bone microstructure generation modeling, was used to partition a plane into several pores after the distribution of pore centers were calculated. Mathematical models were proposed to describe the distribution of pores in tensile specimens. The Fibonacci sequence divides planes or spaces regularly, often found in nature such as sunflowers, pinecones, etc. The Poisson-disc sampling mimics cells growth distribution in two-dimensional plane. The hexagon model is proposed to tile the plane in highly symmetric situation. The regular model and Monte Carlo sampling correspond to a completely regular and completely random distribution models. The porosity variance of specimens was controlled by changing the distribution and quantity of the pores. A series of polymer-based tensile specimens for tensile tests were produced via additive manufacturing. The numerical models were systematically simulated to verify the stress-strain behaviors under physical tensile tests. Extended finite element method cause divergence and errors by the discontinuity of the mesh boundaries and micro-cracks in cellular structures under tensile condition. In this work, lattice spring model was used to simulate micro-cracks generation and propagation. We found when the porosity is 40%, the Poisson-disc sampling and the Fibonacci sequence have higher elongation at break (20% enhancement), ultimate tensile strength (15% enhancement), and toughness (35% enhancement) than other models.

Toughening mechanisms such as crack deflection/tortuosity and uncrack ligament bridging were observed and validated. This research proposes a feasible analysis of lightweight structures, tensile measurement methods, and developed bio-inspired structural materials that can be potentially applied to structural engineering, civil engineering, and aerospace technology.

Acknowledgments:
This research was supported by the Ministry of Science and Technology, Taiwan, R.O.C. (107-2218-E-007-049)
Shape-transformation is a prevalent function observed in living systems, from moisture responsive plants that self-disperse seeds, to muscle actuation by calcium concentration within myocytes. A number of classes of synthetic materials, which mimic this natural behavior, have been developed that use physical or chemical stimuli such as temperature or pH to cause shape changes. However, these stimuli are not specific to the material and may affect various components of the surrounding environment. Additionally, these materials lack the ability of living organisms to respond to specific biomolecular cues and respond accordingly. Here we use the tools of synthetic biology to create living composites capable of responding to pre-determined and very specific stimuli (e.g. biomolecules). Specifically, we present a new method to create programmable shape-morphing living composites using polyacrylamide hydrogels that encapsulate Saccharomyces cerevisiae yeast cells. Proliferation of these microorganisms is controlled to cause the macroscopic shape of the polymer matrix to change (volume expansion up to 300%). As the composite only changes shape in the presence of an appropriate growth media, composites that sense and respond to changes in glucose concentration or the presence of an essential amino acid (e.g. histidine) can be fabricated. Moreover, we utilize optogenetic tools to regulate DNA transcription upon light illumination in modified yeast strains. Shape-change of the composite and proliferation of cells can be spatially and temporally controlled using low power blue light. This extracellular cue induces protein expression in cells and can be used to pattern shape changes in the material. Additionally, the use of these tools enables precise and directional control of shape-morphing with potential applications in tissue engineering, sensing, and drug delivery systems.

References:

11:15 AM SM07.06.06

Designing for Disorder—The Mechanical Behaviour of Bioinspired, Stochastic Honeycomb Materials

Derek Araznour van Esmond, Benjamin D. Hatton and Glenn D. Hibbard; Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada.

In nature, structure, material and function are constantly evolving in tandem. This work employs polymer additive manufacturing to study the mechanical properties of new honeycomb materials inspired by disordered, hierarchical architectures in bioinspired organisms. Inorganic structural features encountered throughout biology are particularly fascinating due to their mechanical resilience and toughness, which arise despite limitations in the available molecular phases of environmental precursors. From very basic and often brittle building blocks, nature has found ways to extend material performance beyond the compositional limitations of its biomineral constituents, e.g. calcium carbonate, apatite and silica. Such improvements have been shown to rely in part on the architectural arrangement of the inorganic phase, which is often non-periodic. This is exemplified in the spongy trabecular bone of load-bearing mammalian limbs, the arrangement of aragonite platelets in the nacre system, and the cellular sandwich-core morphology of biosilica in diatom frustules. The primary aim of this work is thus to elucidate the mechanical role of structural order vs. disorder in natural cellular solids by way of a bioinspired polymer analogue. New honeycomb materials are proposed with improved damage tolerance. A mathematical Voronoi “regularity parameter” controls the degree of cell stochasticity. Uniaxial tension, compression and fracture experiments reveal significant crack path deviations and strain delocalization. These lead to enhancements in e.g. ductility and fracture toughness, \( K_c \), between 30-90% beyond equivalent periodic hexagonal geometries. Optimal cell irregularities are suggested, revealing a relationship between damage tolerance and cell size. Conserving spatial relative density, honeycombs with members composed of hierarchical micro-trusses are also presented. Depending on design objective, a 100% increase in compressive strength and three-fold energy absorption limits \( U_c \) have been achieved. These results comprise novel design spaces, where disorder and hierarchy are capitalized as design variables. Capitalizing on the spatial manufacturing freedom afforded by a modern MultiJet 3D printing technique, iterative tailoring of cell regularity and micro-truss architecture in the honeycomb enables new pursuits toward minimization of energetic tradeoffs. The result is a balance between high stiffness, high weight and damage tolerance from an otherwise brittle constituent polymer.

11:30 AM SM07.06.07

Dynamic Structural Color from Iridescent Bacteria

Clareeta J. Sullivan1, Chia Hung1, Joseph Tang1, Kennedy Brown1, Isaiah Weidmann1, Vincent Chen1, Vincent Tondiglia1, Pam Lloyd1, Miliana C. Vasseu2, Abigail Juhi1, Wendy Goodson1 and Patrick B. Dennis1; 1Materials and Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio, United States; 2University of Massachusetts Dartmouth, Dartmouth, Massachusetts, United States.

Biofilms from the marine bacteria, Cellulophaga lytica, have been reported to display structural, iridescent colors that were found to be both reversible and dynamic. Here we present several scientific and technological advances using micro-spectral imaging, confocal microscopy, angle-dependent reflection measurements and atomic force microscopy. To facilitate these studies, we have successfully fixed C. lytica colonies which remain stable iridescent for months. Micro-spectral imaging revealed angle-dependent reflection in the blue, green, yellow, orange and red structural color regions. Since cells displayed a similar size in all structural color regions, the different reflected colors likely came from different crystalline planes and/or periodicities. Cross-section images of C. lytica in the different colored regions demonstrated highly-ordered end-to-end assembly of hexagonal photonic crystals through crystalline plates, and the small refractive index mismatch between the bacteria and aqueous environment explains the small angle reflection peaks. Together, our studies imply that C. lytica is an excellent light scatterer that reflects different wavelengths of light through self-organization. Moreover, since our studies focused on a C. lytica strain with a known genomic sequence, future synthetic biology approaches will be aimed at producing low-cost, tunable photonic crystals based on programmable, self-assembling microorganisms for optical and sensor applications.

11:45 AM SM07.06.08

Facile Fabrication of Dry Adhesives Based on Hierarchical Fibrillar Structure of Poly (Dimethyl Siloxane) (PDMS)

Sung-Ryong Kim, Wu M. Canh and Nhat Anh T. Thieu; Korea National University of Transportation, Chungu, Korea (the Republic of).

We present a simple and low cost method of utilizing nanosized anodized aluminium oxide (AAO) and microsized silicon membrane as a reproducible template to prepare hierarchical fibrillar poly (dimethyl siloxane) (PDMS) dry adhesives that can be used as a medical patch. On the contrary to the adhesives containing only micrometer-size fibrils, the hierarchical fibrillar adhesives exhibited a higher adhesion force. Normal adhesion force on the glass substrate was higher than 8 N/cm² and this value was higher than that of homogenous PDMS micropillars. The successful fabrication of such hierarchical adhesive could be potentially used in applications requiring repetitive adhesion without significant loss of adhesion strength.

1:30 PM SM07.07.01

Bioinspired Extrinsic Control of Freeze Casting

Steven Naleway, Isaac Nelson, Anthony Yin, Max Mroz and Paul Wadsworth; University of Utah, Salt Lake City, Utah, United States.

Freeze casting is a bioinspired technique for the fabrication of tailored, porous ceramic materials. Mimetic of the growth of mammalian bone and other biomaterials where biopolymers template the deposit of biominerals to create complex composites, freeze casting employs a template of growing ice crystals to create a complex porous microstructure in any ceramic. We propose that this bioinspired technique can be controlled through either intrinsic (those that modify from within by altering the constituents) or extrinsic (those that apply external forces or templates) means. Through these classifications, examples of extrinsic (through energized external fields) freeze cast, bioinspired structures will be discussed with a focus on providing advanced control of the final material structure and properties. Applications in energy and filtration technologies will be...
Helmholtz coil-based freeze casting setup is used to control the fabrication of porous structures. With this setup, a magnetic field can be created in any direction which is utilized to optimize the alignment of biopolymers. When functional ceramics are added to the initial PVA slurry, which increases the diversity of material selection and extensive potential applications. This research is funded by the Ministry of Science and Technology, Taiwan (MOST 103-2221-E-007-034-MY3).

The structure of many biological materials is hierarchical in nature meeting specific needs at each length scale. This includes human bone, which has a porous structure that plays a critical role in arresting crack growth, energy absorption and mechanical strength in specific loading directions. In this research, a novel tri-axial nested Helmholtz coil-based freeze casting setup is used to control the fabrication of porous structures. With this setup, a magnetic field can be created in any direction which is utilized to manipulate particles to align the microstructure. The ability to control the particle alignment results in user-specific mechanical properties at user-specific locations. These structures provide a path to better mimic the mechanical characteristics seen in human bone.

Freeze Casting Using a Tri-Axial Nested Helmholtz Coil to Fabricate User-Specific Porous Scaffolds

Isaac Nelson, Max R. Mroz, Anthony Yin, Paul Wadsworth and Steven Naleway; University of Utah; Salt Lake City, Utah, United States.

Regulation of Apatite Biomineralization in the Mantis Shrimp Dactyl Club by a Newly Discovered Protein, CMP-1

Hortense Le Ferrand1, Shahrouz Amini1, Maryam Tadayon1, Jun Jie Loke1, Akshita Kumar1, Deepankumar Kanagavel1, Martial Duchamp1, Manfred Raida1, Shawn Hoon1 and Ali Miserez2; 1Nanyang Technological University, Singapore, Singapore; 2National University of Singapore, Singapore, Singapore; 3A*STAR, Singapore, Singapore.

The dactyl club of the mantis shrimp (stomatopod) is a fascinating example of a highly organized hierarchical hard composite material that combines strength and toughness. Another peculiar feature of this appendage lies in its formation process through molting cycles: as a crustacean mantis shrimps grow an entirely defect-free functional exoskeleton within just a few weeks. This feature makes the mantis shrimp an ideal model organism to monitor biomineralization processes. In this study, a protein from the club (club Mineralization Protein 1, CMP-1) was identified and sequenced using a combined transcriptomics/proteomics approach, and shown to regulate calcium phosphate mineralization of the club. After recombinantly expressing CMP-1, we show that CMP-1 can form dense organic microdroplets through liquid-liquid phase separation induced by calcium ions. Furthermore, in vitro experiments with TEM demonstrate that CMP-1 can participate in the formation of precursor-like amorphous calcium phosphate granules that subsequently grow into preferentially oriented crystalline apatite nanofibers.

This work not only corroborates recent observations made in other systems that proteins regulating biomineralization can initially undergo phase separation [3], but also provides a comprehensive picture of key steps involved in the growth of a mechanically functional highly mineralized composite. The study thus offers guidelines for advanced bioinspired manufacturing methods for strong and tough ceramic-organic composites.


SYMPOSIUM X

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Research in the Stevens Programme focuses on designing and developing innovative bio-inspired materials for applications in regenerative medicine, tissue engineering and the design of materials for ultrasensitive biosensing, applying these nanomaterial-based approaches to high throughput drug screening and to diagnose diseases.

Biography: Molly M. Stevens is currently Professor of Biomedical Materials and Regenerative Medicine, Research Director for Biomedical Material Sciences in the Department of Materials, Department of Bioengineering and the Institute of Biomedical Engineering at Imperial College London, and Director of the UK Regenerative Medicine Programme Hub for Smart Materials. She received her PhD from The University of Nottingham in 2000, then conducted her postdoctoral research at MIT in the labs of Prof Robert Langer, where she co-developed innovative techniques for the regenerative of bone and other tissues. She joined Imperial College in 2004 and was promoted to Full Professor in 2008. Research in the Stevens Programme focuses on designing and developing innovative bio-inspired materials for applications in regenerative medicine, tissue engineering and biosensing. Her research has been recognised by over 20 major awards. More information on the Stevens Group can be found at http://www.stevensgroup.org.

**SESSION X.01**

12:15 PM *X.01.01*

**Designing Bio-Responsive Hybrid Materials**

Molly Stevens; Imperial College London, London, United Kingdom.

**Abstract:** Bio-responsive hybrid materials are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering. A side effect of longer life-spans is the failure of one part of the body. The search for replacement body parts has fuelled the highly interdisciplinary field of tissue engineering and regenerative medicine. This talk will describe our research on the design of new hybrid (nano)materials and nanomaterials to direct stem cell differentiation for regenerative medicine. We have also designed and developed porous silicon “nanoneedles” capable of efficiently, rapidly and safely delivering sensitive biocargoes to cells and tissues in vivo as well as interfacing with cells to inform intracellular pH and high resolution demarcation of tumorous region boundaries. This talk will also provide an overview of our recent developments in the design of materials for ultrasensitive biosensing, applying these nanomaterial-based approaches to high throughput drug screening and to diagnose diseases.

**Biography:** Molly M. Stevens is currently Professor of Biomedical Materials and Regenerative Medicine, Research Director for Biomedical Material Sciences in the Department of Materials, Department of Bioengineering and the Institute of Biomedical Engineering at Imperial College London, and Director of the UK Regenerative Medicine Programme Hub for Smart Materials. She received her PhD from The University of Nottingham in 2000, then conducted her postdoctoral research at MIT in the labs of Prof Robert Langer, where she co-developed innovative techniques for the regenerative of bone and other tissues. She joined Imperial College in 2004 and was promoted to Full Professor in 2008. Research in the Stevens Programme focuses on designing and developing innovative bio-inspired materials for applications in regenerative medicine, tissue engineering and biosensing. Her research has been recognised by over 20 major awards. More information on the Stevens Group can be found at http://www.stevensgroup.org.

**SESSION X.02**

12:15 PM *X.02.01*

**Hydrogen and Fuel-Cell Technology Perspectives**


Today the technology around generating efficient and sustainable energy is rapidly evolving and hydrogen and fuel cells are versatile examples within a portfolio of options. This presentation will provide an overview of the U.S. Department of Energy’s Fuel Cell Technologies Office early-stage R&D activities in hydrogen and fuel cells within the Office of Energy Efficiency and Renewable Energy. Dr. Satyapal will highlight technology status and progress towards achieving DOE targets, discuss R&D needs and challenges, and provide specific examples where advanced materials research is relevant to address those challenges. The presentation will also cover DOE’s H2@Scale initiative which will enable innovations to generate cost-competitive hydrogen as an energy carrier, coupling renewables, as well as nuclear, fossil fuels, and the grid, to enhance the economics of both baseload power plants and intermittent solar and wind, enhancing resiliency and avoiding curtailment.

Sunita Satyapal is the Director for the U.S. Department of Energy’s (DOE) Fuel Cell Technologies Office within the Office of Energy Efficiency and Renewable Energy. She is responsible for the overall strategy, program execution and staff in the area of hydrogen and fuel cell technologies, including oversight and coordination of approximately $100 million per year in research, development, demonstration and deployment activities. Dr. Satyapal has more than 20 years of experience in academia, industry and government and has 10 patents issued. She received her Ph.D. from Columbia University and did her postdoctoral work in Applied and Engineering Physics and Physical Chemistry at Cornell University.

**SESSION X.02**

12:40 PM *X.02.02*

**Development of Fuel Cells and Hydrogen Technologies in Europe Toward Commercialization from 2020 Onward**

Bart Biebuyck; The Fuel Cells and Hydrogen Joint Undertaking, Brussels, Belgium.

The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) was set up in 2008 to accelerate the development of fuel cells and hydrogen (FCH) technologies in Europe toward commercialization from 2020 onwards. To reach this target the FCH JU brings together resources under a cohesive public-private partnership to ensure commercial focus, to match RTD activities to industry's needs and expectations and to scale-up and intensify links between the Industry Community and the Research Community. The FCH JU support stretches from research and demonstration projects in the different areas of FCH including energy and transport applications. The €893 million in grants already allocated under the FCH JU support provides specific examples where advanced materials research is relevant to address those challenges. The presentation will also cover DOE’s H2@Scale initiative which will enable innovations to generate cost-competitive hydrogen as an energy carrier, coupling renewables, as well as nuclear, fossil fuels, and the grid, to enhance the economics of both baseload power plants and intermittent solar and wind, enhancing resiliency and avoiding curtailment.

Bart Biebuyck is the Executive Director of the Fuel Cells and Hydrogen Joint Undertaking (FCH JU), a public-private partnership aiming at facilitating the deployment of fuel cells and hydrogen technologies in Europe. Before the FCH JU, Bart Biebuyck was at the Fuel Cell department of Toyota Motor Europe where he held the position of Technical Senior Manager. His expertise in the automotive industry includes extensive knowledge related to the deployment of new technologies in the European market. It is as part of the Clean Energy Partnership (CEP) programme in Berlin that Bart worked at reinforcing European trials for the Toyota Fuel Cell Hybrid Vehicle. He also had the opportunity to develop and expand his knowledge in Japan, where for two years he worked on the PSA-Toyota Small Vehicle Development Project which resulted in the launch of the Toyota AYGO in 2006. In addition to his industrial experience, Bart has been politically active in his local town since 2006. In 2013 he became the vice president of the City Council, responsible, among others, for the local economy and education. Bart joined the FCH JU as the new Executive Director on the 16 May 2016.
This talk introduces the James Webb Space Telescope, NASA’s next large astrophysics mission. Webb’s science goals; detection of the universe’s first light, assembly of galaxies, birth of stars and observation of planets and exo-planets are introduced. We will explore how the design responds to mission requirements and produces the performance necessary to achieve the mission’s goals. Many of the unique elements of the architecture will be explored. The main engineering challenges for largest telescope ever built in space are discussed and the role of materials highlighted. Finally, the current status of the hardware and path to launch will be given.

Jonathan Arenberg is currently the Chief Engineer for Space Science Missions at Northrop Grumman Aerospace Systems. Dr. Arenberg has worked the Chandra X-ray Observatory and James Webb Space Telescope. He co-conceived and developed the Starshade concept for the direct imaging of extra-solar planets and other innovative mission concepts. He has worked on laser systems and component engineering, metrology, inspection issues and technology development. He is a member of US National and International committees charged with writing standards for laser and electro-optic systems and components, SPIE, American Astronomical Society, AAAS, AIAA and Sigma Xi. Dr. Arenberg holds a BS in physics and an MS and PhD in engineering, all from the University of California, Los Angeles. He is the author of over 180 conference presentations, papers and book chapters and a recent book. He holds a dozen European and U.S. Patents in various areas of technology and is an SPIE Fellow.